

50X1-HUM

Page Denied

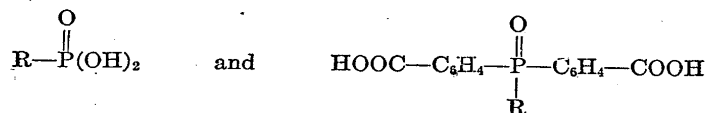
Next 1 Page(s) In Document Denied

Some Special Features of Organic Polymers Containing Phosphorus

V. V. KORSHAK, *Institute of Hetero-Organic Compounds, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.*

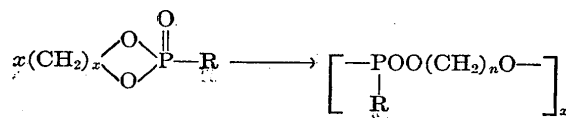
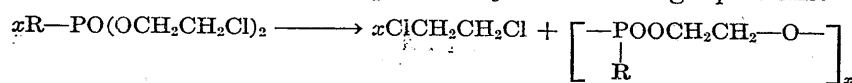
STAT

Organophosphorus polymers being a new class of compounds, their systematic study has only recently been begun. This paper deals with some special properties of a number of organophosphorus polymers which were prepared by us and compared with properties of similar polymers which do not contain phosphorus in their molecules. These organophosphorus polymers belong to the class of polyesters or polyamides. Various alkyl- and arylphosphinic acids and also dicarboxytriphenylalkyl- or -arylphosphine oxides were used to prepare the polyesters. The starting phosphorus-containing dicarboxylic acids were of the following two types:



where: $\text{R} = \text{CH}_3, \text{ClCH}_2, \text{C}_6\text{H}_5, \text{C}_4\text{H}_9$, and others. However, in view of the low reactivity of these acids, only their derivatives, such as chloroanhydrides or dimethylesters, were used. Aliphatic glycols and diphenols were used as the second component.

Polyesters were also prepared by polycondensation of β -chloroethylesters of alkyl- and arylphosphinic acids,¹ and also by polymerization of cyclic esters of these acids, as it has been formerly described.² The reactions proceeding in these two cases are expressed by the following equations:



To prepare polyamides, dicarboxytriphenylalkyl- and -arylphosphine oxides and various aliphatic diamides were used. The reaction of polycondensation has been carried out according to a method previously described.³

Table I summarizes the formulas of some polyesters we have obtained from alkyl- and arylphosphinic acids and aliphatic glycols with their softening temperatures.

TABLE I

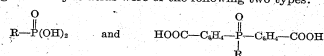
Structural unit	Softening temperature, °C.
$\begin{array}{c} \text{O} \\ \\ -\text{P}-\text{OCH}_2\text{CH}_2\text{O}- \end{array}$	-35

Some Special Features of Organic Polymers Containing Phosphorus

STAT

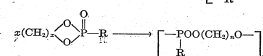
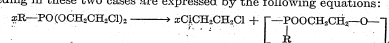
V. V. KORSHAK, *Institute of Hetero-Organic Compounds, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.*

Organophosphorus polymers being a new class of compounds, their systematic study has only recently been begun. This paper deals with some special properties of a number of organophosphorus polymers which were prepared by us and compared with properties of similar polymers which do not contain phosphorus in their molecules. These organophosphorus polymers belong to the class of polyesters or polyamides. Various alkyl- and arylphosphinic acids and also dicarboxytriphenylalkyl- or -arylphosphine oxides were used to prepare the polyesters. The starting phosphorus-containing dicarboxylic acids were of the following two types:



where: $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$, and others. However, in view of the low reactivity of these acids, only their derivatives, such as chloroanhydrides or dimethylesters, were used. Aliphatic glycols and diphenols were used as the second component.

Polyesters were also prepared by polycondensation of β -chloroethyl esters of alkyl- and arylphosphinic acids,¹ and also by polymerization of cyclic esters of these acids, as it has been formerly described.² The reactions proceeding in these two cases are expressed by the following equations:



To prepare polyamides, dicarboxytriphenylalkyl- and -arylphosphine oxides and various aliphatic diamides were used. The reaction of polycondensation has been carried out according to a method previously described.³

Table I summarizes the formulas of some polyesters we have obtained from alkyl- and arylphosphinic acids and aliphatic glycols with their softening temperatures.

TABLE I

Structural unit	Softening temperature, °C.
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{OCH}_2\text{CH}_2\text{O}- \\ \text{CH}_3 \end{array}$	-35
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}- \\ \text{CH}_3 \end{array}$	-35
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}- \\ \text{CH}_3 \end{array}$	-63
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{O}(\text{CH}_2)_4\text{O}- \\ \text{CH}_3 \end{array}$	-65
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{O}(\text{CH}_2)_6\text{O}- \\ \text{CH}_3 \end{array}$	-35
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{O}(\text{CH}_2)_8\text{O}- \\ \text{CH}_3 \end{array}$	58
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}- \\ \text{CH}_3 \end{array}$	-50

TABLE II

Structural unit	Softening temperature, °C.
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{O}-\text{C}_6\text{H}_4-\text{O}- \\ \text{CH}_3 \end{array}$	63
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{O}-\text{C}_6\text{H}_4-\text{O}- \\ \text{C}_6\text{H}_5 \end{array}$	83
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{O}-\text{C}_6\text{H}_4-\text{O}- \\ \text{O} \end{array}$	19
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{O}-\text{C}_6\text{H}_4-\text{O}- \\ \text{C}_6\text{H}_5 \end{array}$	36
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{O}-\text{C}_6\text{H}_4-\text{O}- \\ \text{OC}_6\text{H}_4\text{NO}_2 \end{array}$	63
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{O}-\text{C}_6\text{H}_4-\text{O}- \\ \text{OC}_6\text{H}_4\text{OCH}_3 \end{array}$	36
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{O}-\text{C}_6\text{H}_4-\text{O}- \\ \text{CH}_3 \end{array}$	55
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{O}-\text{C}_6\text{H}_4-\text{O}- \\ \text{CH}_3 \end{array}$	88
$\begin{array}{c} \text{O} \\ \parallel \\ \text{P}-\text{O}-\text{C}_6\text{H}_4-\text{O}- \\ \text{CH}_3 \end{array}$	55

As will be seen from Table I, these polyesters have very low softening temperatures. Their outward appearance is that of thick Vaseline-like materials.

Table II summarizes the polyesters of alkyl- and arylphosphinic acids with such diphenols as hydroquinone, resorcinol, and *p,p'*-dihydroxydiphenyl propane. They are solid, elastic, or brittle vitreous substances. Their melting points are much higher than with polyesters of aliphatic glycols.

TABLE III

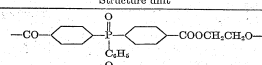
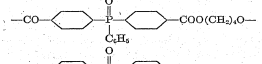
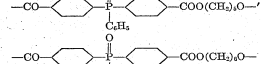
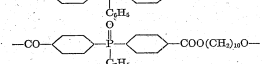
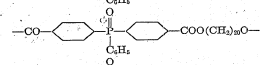
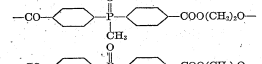
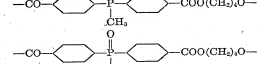
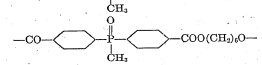
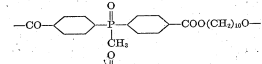
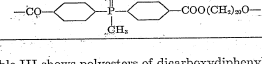
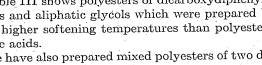
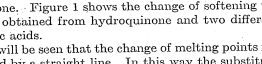
Structure unit	Softening temperature, °C.
	190
	144
	128
	90
	101
	50
	155
	128
	93
	60
	67
	120

Table III shows polyesters of dicarboxydiphenylalkyl- or -arylphosphine oxides and aliphatic glycols which were prepared by us. These polyesters have higher softening temperatures than polyesters of alkyl- or arylphosphinic acids.

We have also prepared mixed polyesters of two different acids and hydroquinone. Figure 1 shows the change of softening temperatures for copolymers obtained from hydroquinone and two different alkyl- and arylphosphinic acids.

It will be seen that the change of melting points in these systems is represented by a straight line. In this way the substitution of a phenyl radical by an alkyl one does not lead to a minimum on the curve "composition vs. properties" as is usually observed with mixed polyesters.

Table IV summarizes the polyamides of dicarboxydiphenylalkyl- and -arylphosphine oxides and aliphatic diamines. These compounds have higher melting temperatures than corresponding polyesters.

TABLE IV

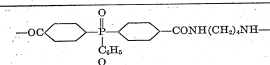
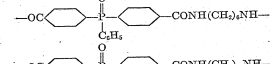
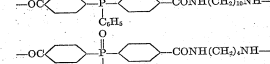
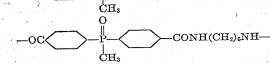
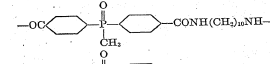
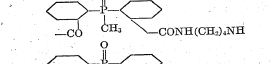
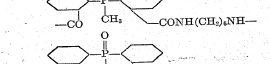
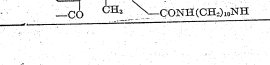

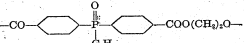
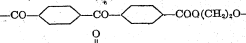
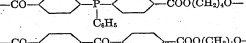
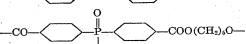
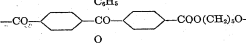
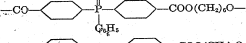
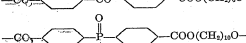
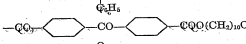
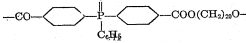
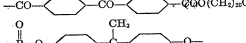
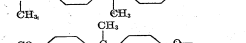
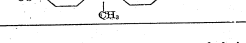
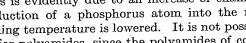
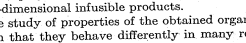
Structural unit	Softening temperature, °C.
	195
	190
	150
	180
	170
	140
	128
	109
	94

Figure 2 shows the change of softening temperature of mixed polyamides prepared from hexamethylene diamine, dicarboxytriphenylphosphine oxide and adipic acid or caprolactam. These curves show clearly the presence of a minimum on the melting point curve. This minimum occurs for a copolymer containing 20 or 40 mole % of the longer component. This is usually observed also with other mixed polyamides.⁴

Inspection of all these data shows that polyesters and polyamides of the types investigated, which contain a phosphorus atom in their molecule, have lower softening temperatures than polyesters and polyamides of dicarboxylic acids of related structure whose molecules contain an atom of carbon instead of phosphorus.

Table V summarizes, for comparison, softening temperatures of some compounds obtained by us and closely related to corresponding polyesters of organophosphorus dicarboxylic acids.⁴ It is seen that the introduction of a phosphorus atom causes a substantial depression of the softening temperatures of the polyesters.

TABLE V

Structural unit	Softening temperature, °C.
	177
	318
	144
	168
	138
	66
	90
	129
	109
	98
	60
	100
	88
	220

This is evidently due to an increase of chain flexibility induced by the introduction of a phosphorus atom into the macromolecule. Thus the softening temperature is lowered. It is not possible to present comparable data for polyamides, since the polyamides of corresponding keto-acids are three-dimensional infusible products.

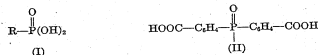
The study of properties of the obtained organophosphorus polymers has shown that they behave differently in many respects. It is necessary to point out in the first place that they have a much higher elasticity in comparison with corresponding polyesters and polyamides of dicarboxylic acids which do not contain phosphorus. Also, they are not inflammable, and this is also evidently due to the presence of phosphorus in their molecules.

References

1. V. V. Korshak, I. A. Gribova, and V. K. Shitikov, *IX Conference on General Problems of Chemistry and Physics of High Molecular Compounds*, Theses of papers, Ed. by Acad. Sci. of the U.S.S.R., Moscow, 1956, p. 9.
2. V. V. Korshak, I. A. Gribova, and M. A. Andreeva, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1957, 631.
3. V. V. Korshak and T. M. Frunze, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1955, 163.
4. V. V. Korshak and T. M. Frunze, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1955, 372.
5. V. V. Korshak, S. V. Vinogradova, and T. M. Frunze, *Zhur. Obshch. Khim.*, 27, 1600 (1957).

Synopsis

Results obtained in the investigation of polymers containing pentavalent phosphorus in the main polymer chain are presented. A number of polyamides and polyesters derived from phosphorus-containing dicarboxylic acids have been synthesized. Two types of dicarboxylic acids were used: alkyl- or aryl-phosphinic acids (I) and bis-carboxyphenylphosphine oxides (II):



their chloroanhydrides or esters being used in the reaction. To obtain polyesters, various glycols or dihydric phenols were used as the second component. For preparing polyamides, aliphatic diamines were used as the second component. The nature of the starting materials has a very marked effect on the properties of the polymers obtained. Polyesters with an aliphatic chain are viscous, thick oils or low-melting resins. Polyesters with aromatic unit are high-melting, solid elastic substances. Comparison of the properties of the polymers synthesized by us with the properties of polymers of related composition not containing phosphorus, shows that the introduction of phosphorus into the chain leads to molecules of much greater flexibility. For this reason the softening points of the phosphorus-containing polymers are much lower than those of their carbon analogues.

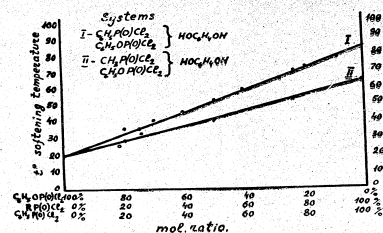


Fig. 1. Softening temperatures of mixed polyesters of hydroquinone and alkyl- or arylphosphinic acids. (I) System obtained from hydroquinone and chloroanhydrides of phenylphosphinic and hydroxyphenylphosphinic compound. (II) System prepared from hydroquinone and chloroanhydrides of methylphosphinic and phenyloxyposphinic acids.

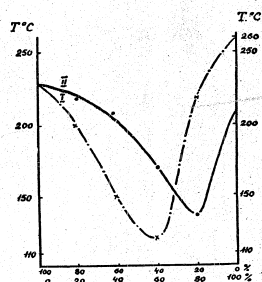


Fig. 2. The depression of melting points of mixed polyamides. (I) System composed of salts of hexamethylene diamine and of both adipic acid and p,p' -dicarboxytriphenylphosphine oxide. (II) System composed of a salt of hexamethylene diamine and p,p' -dicarboxytriphenylphosphine oxide, and caprolactam.

Polymerization of Aromatic and Heterocyclic Vinyl Compounds

STAT

M. M. KOTON, *Institute of Macromolecular Compounds, Academy of Sciences of the U.S.S.R., Leningrad, U.S.S.R.*

STAT

A considerable quantity of substituted ethylenes and the wide possibilities of their application for practical usage made them of extensive interest for the investigator. The study of the influence of chemical structure of vinyl series monomers upon their polymerization ability is both interesting from the scientific point of view and important for practical purposes. However, by reviewing the bibliography on the polymerization of vinyl compounds, one observes that the number of systematic investigations in comparable conditions that enable evaluation of the influence of the properties of substituting groups in ethylene molecules on the polymerization process, is not all sufficient. Among the great number of ethylene series derivatives, its aromatic derivatives have long been drawing the attention of investigators. The studies of Shorygin,¹ Marvel,² Wiley,³ as well as our data⁴ show that within the series of substituted styrenes there is interrelation between the structure of monomers and their ability for polymerization. The rate of polymerization of substituted styrenes differs, depending on the chemical nature of the substituents, the number of substituents, and their position in the styrene benzene ring as related to the vinyl group. We⁴ have studied some substituted styrenes (halogen- and methylstyrenes) and have shown the influence of isomerism of substituents in the styrene benzene ring upon the rate of polymerization which increases from mono- to di- and tri-substituted styrenes. Polymerization of substituted styrenes, when such substituents as halogen atoms and the cyano-group are introduced, proceeds with greater speed because the process of polymerization continues less actively (8-15 cal/mole) compared to unsubstituted styrene (22 cal/mole). The study of the polymerization ability of other aromatic and heterocyclic substituents of ethylene encounters many difficulties, mostly because it is rather complicated to isolate these monomers in their pure form since they polymerize very easily.

POLYMERIZATION OF VINYL COMPOUNDS OF THE NAPHTHALENE SERIES

We thought that it would be most interesting to connect the high reactivity of vinyl compounds of multinuclear hydrocarbons with the existence of coupling double bonds in the rings, giving as examples certain vinyl compounds of the naphthalene series.

With this purpose we have synthesized: (1) vinylnaphthalene (1-VN), b.p. 86-88°C. (2 mm.), n_D^{20} 1.6405; (2) vinylnaphthalene (2-VN), m.p. 65-66°C. dibromide melting point 83.4°C., 6-vinyl-1,2,3,4-tetrahydronaphthalene (VT), b.p. 96-98°C. (2 mm.), n_D^{20} 1.5690.

The content of monomer in all these compounds was 96.6-99.8%.

Vinyldecahydronaphthalene (VD) was isolated for the first time, in the same way as VT, as a colorless liquid, b.p. 103°C. (3 mm.), n_D^{20} 1.5443.

Vinyl substituents of naphthalene were polymerized in a block at 100, 110, and 125°C.

The studies of Koton and Kiseleva⁵ showed that 1-VN and 2-VN have the greatest rate of polymerization, the 1-VN being the easiest to polymerize. VT is much slower to polymerize, being more like unsubstituted styrene (Fig. 1). VD, which has no double bonds in the monomer molecule ring, did not polymerize during thirty days at 100°C. The obtained polymers were of low molecular weight and had the following value of $[\eta]$: 1-VN, 0.06; 2-VN and VT, 0.22.

The study of polymerization kinetics provided data for the calculation of the value of activation energy of polymerized vinyl derivatives in the naphthalene series: 1-VN, 16.9 ± 0.5 kcal/mole; 2-VN, 18.8 ± 0.3 kcal/mole; and VT, 20.9 ± 0.5 kcal/mole. Thus, vinyl derivatives of the naphthalene series showed that there is a relationship between the number of coupling double bonds in the monomer molecule ring and the polymerization ability.

POLYMERIZATION OF VINYL DERIVATIVES OF PYRIDINE AND QUINOLINE

To acquire more data on the polymerization process of vinyl compounds which contain different cyclic radicals as substituents in ethylene molecule, we have studied 2-vinylpyridine (VP) and 2-vinylquinoline (VQ). We have chosen these particular monomers because they enabled us to compare the data on their polymerization with those of styrene and 2-vinyl-naphthalene we had obtained before, and thus to evaluate the influence of a heteroatom (nitrogen), which is a part of the cyclic radical, upon polymerization ability. Besides this, the polymerization of VQ has been studied very little until now.⁶ VP was isolated according to the Winterfeld and Heinen method,⁷ its properties are b.p. 64.5°C. (2 mm.); n_D^{20} 1.5497; n_D^{20} 0.9757; n_D^{20} 34.32.

VQ was isolated by means of the Bachmann and Micucci method.⁷ Its properties are b.p. 104°C. (3 mm.); n_D^{20} 1.0705, n_D^{20} 62.78.

The polymerization process of these monomers was studied by Surnina,¹² and was carried out in a block in the presence of azobisisobutyronitrile (0.135 mole-%) as the initiator in a nitrogen atmosphere. Polymerization was carried out dilatometrically at 50, 55, 60, 75, and 90°C.

As Figures 2 and 3 show, VP is polymerized faster than styrene and VQ. In 30 minutes at 60°C. the yield of VP was 10.6% and of styrene, 1.7%. VQ yielded 6.4% in 15 minutes at 90°C.

The determined $[\eta]$ values were: VP, 0.5; VQ, 0.1. The data on polymerization kinetics were used to calculate the activation energy of polymerization: VP, 20 ± 1 kcal/mole; VQ, 18 ± 1 kcal/mole. For a more thorough evaluation of the reactivity of VP and VQ, we have studied their polymerization with unlimited monomers. Copolymerization was effected in the presence of azo-bis-isobutyronitrile (0.2%) at 60°C.

The composition of copolymers was determined by the Dumas micro-determination of nitrogen.

Copolymerization constants were determined with the help of integral equation of copolymer composition; the data are shown in Table I.

TABLE I
Constants of Copolymerization of 2-Vinyl Pyridine and 2-Vinyl Quinoline with Some Monomers

No.	M_1	M_2	r_1	r_2
1	2-Vinyl pyridine	Styrene	1.81 ± 0.05	0.55 ± 0.03
2	"	Isoprene	0.47 ± 0.07	0.59 ± 0.05
3	"	Chloroprene	0.06 ± 0.01	5.19 ± 0.03
4	"	Acrylonitrile	21.88 ± 5.52	0.05 ± 0.01
5	2-Vinyl quinoline	Styrene	2.09 ± 0.55	0.49 ± 0.14
6	"	Isoprene	1.38 ± 0.02	0.33 ± 0.01
7	"	Chloroprene	0.38 ± 0.03	2.10 ± 0.02

M. M. KOTON

The system VP-isoprene allows isolation of azeotropic copolymer. We must also point out the system VP-acrylonitrile which is like the well-known system vinyl styrene-acetate. Monomer VP couples with both types of radicals 20-22 times faster than with acrylonitrile.

The determined constant values of copolymerization allowed calculation of the activity of VP and VQ monomers as related to styrene, isoprene, chloroprene, and acrylonitrile radicals as shown in Table II.

TABLE II
Activity of 2-Vinyl Pyridine and 2-Vinyl Quinoline as Related to Different Radicals

Monomers	Radicals					
	2-vinyl pyri- dine	2-vinyl quino- line	Sty- rene	Isop- rene	Chloro- prene	Acrylo- nitrile
2-Vinyl pyridine	1.0	—	1.8	1.7	0.2	21.7
2-Vinyl quinoline	—	1.0	2.0	1.8	0.5	—
Styrene	0.5	0.5	1.0	0.5*	0.14*	20.0*
Isoprene	2.1	0.5	0.7*	1.0	0.27*	33.3*
Chloroprene	16.6	2.6	20.0*	7.5*	1.0	100*
Acrylonitrile	0.05	—	2.7*	2.2*	0.17*	1.0

* Data obtained by other authors.

The data of Table II show that VQ is more active than VP, while the latter is more active than styrene. Thus the results of the studies of VP and VQ polymerization are in the same relation as the results obtained for styrene and 2-vinyl naphthalene.

POLYMERIZATION OF VINYL DERIVATIVES OF FURAN AND THIOPHENE

To obtain more detailed data on the influence of the nature of heteroatoms which constitute cyclic radicals of substituted ethylenes upon the polymerization process, Andreyeva and Koton¹³ have studied some vinyl derivatives of the furan and thiophene series which up till now have been but little studied. For this purpose they synthesized: 2-vinyl furan (VF), b.p. 96-97°C., n_D^{20} 1.4994; 2-vinyl thiophene (VT), b.p. 66.5°C. (48 mm.), n_D^{20} 1.5722; 2-vinyl benzofuran (VBF) b.p. 52°C. (0.5 mm.), n_D^{20} 1.6020; 2-vinyl dibenzofuran (VDBF), b.p. 130°C. (0.5 mm.), m.p. 31°C.; and 2-vinyl dibenzothiophene (VDBT), m.p. 42°C. These compounds had 99.7-99.9% of monomer.

Andreyeva and Koton have studied the polymerization process for all monomers of the furan and thiophene series in the presence both of peroxides (0.5 mole-% of benzoyl peroxide) and ion catalysts (lithium butyl, boron trifluoride etherate). Polymerization has been carried out in block in benzene and toluene solutions by means of the dilatometric method in the temperature range of 0 to 100°C.

The obtained data on the VF polymerization kinetics at 80, 90, and 100°C. allowed the calculation of activation energy of polymerization process: 17 ± 1 kcal./mole. The observation was made while studying the VF polymerization that molecular oxygen plays an important role in formation of properties of synthesized polymers. In the absence of ambient oxygen, the VF polymerizes with the benzoyl peroxide to form a hard and non-fusible polymer which is obtained in the form of grains of the "co-polymer" type; this type of polymer had been observed by Carothers with co-workers¹⁰ and by Pravednikov and Medvedev¹¹ when studying diene polymerization.

The formation of the three-dimensional polymer leads us to believe that the double bonds in the ring of the VF polymer take part in the polymerization reaction. In the presence of oxygen, instead of these polymers, VF polymers are formed which are a soft mass. Their temperature of softening after resettling is 60-80°C.

Polymerization of VBF has been little studied; there is only one work by Elliott¹² which states that this polymer is able to polymerize and co-polymerize.

Polymerization of VDBF has not been studied at all. Investigations into the polymerization kinetics of these monomers at 60, 80, 90, and 100°C. permitted calculation of activation energy of the VBF polymerization process, 16.5 ± 0.5 kcal./mole, and of VDBF, 12.4 ± 0.60 kcal./mole. The determined values show that the VDBF have a very high reactivity in the polymerization process. These monomers also easily polymerize in the presence of ion catalysts. The VBF in the presence of BF_3 at 0°C. gave a 42% yield of polymer after 3 hours; the VDBF, 70% after 1 hour. The VF polymers had an intrinsic viscosity, $[\eta]$, of 0.02-0.2, the value depending on polymerization conditions. The VDBF polymers had an $[\eta]$ of 0.05-0.40; while the polymers synthesized in the presence of the initiator of 1.44 .

Polymerization of 2-vinyl thiophene (VT) and 2-vinyl dibenzothiophene (VDBT) have been but little studied.^{13,14} These monomers polymerize very easily both in the presence of radical initiators and ion-type catalysts. The VDBF polymerizes more quickly than VT (Fig. 4). The energy of activation of the polymerization process of VT is 16.5 ± 0.5 kcal./mole. VT, together with etherate BF_3 at 0°C., gave a yield of 74% of polymer in 50 minutes, the intrinsic viscosity of VT polymers was 0.08, and the temperature of softening was 70-85°C. The polymers of the VDB showed $[\eta]$ of 0.13-0.20 and a softening point of 144°C.

The results that have been obtained by studying the polymerization of vinyl derivatives of furan and thiophene series show that by increasing the number of condensed rings in the monomer molecule, we can considerably increase the rate of the polymerization process (Fig. 5). The data for the monomers of the same structure of the furan and thiophene series have been compared and the results help to determine the influence of nature of the heteroatom (oxygen, sulfur) upon the ability to polymerize. It was proved that the VT monomer is more reactive than the VF monomer, and under equal conditions it polymerizes twice as quickly as the latter (Fig. 6). The monomers VDBF and VDBT have the same tendency, the only difference being that the influence of the nature of the heteroatom is revealed much less distinctly (Fig. 7), as was observed before with pyridine and quinoline. The monomer studied form series according to their reactivity in polymerization: 2-vinyl furan (thiophene) > 2-vinyl benzofuran > 2-vinyl furan (thiophene), and 2-vinyl thiophene > 2-vinyl furan.

Thus, the results of our investigations show that by increasing the number of condensed rings in the substituting radical of ethylene molecules, and by introducing heteroatoms (nitrogen, oxygen, sulfur) into them, we can heighten the ability of these compounds to polymerize.

STAT

Copy 109-PROD NO P-49-KOTON

STAT

References:

1. P. P. Shorygin and N. V. Shorygina, *Zhur. Obshch. Khim.*, **5**, 555 (1935); **9**, 845 (1939).
2. C. Marvel, *J. Am. Chem. Soc.*, **62**, 45 (1940); **66**, 475 (1944); **67**, 2250 (1945); **68**, 737, 1085, 1088, 1090, 2108 (1946); **70**, 1895 (1948).
3. R. Wiley, *J. Polymer Sci.*, **3**, 445 (1948); **5**, 483 (1950); *J. Am. Chem. Soc.*, **70**, 1500 (1948); **71**, 2429 (1949); **72**, 1822, 5198 (1950); **75**, 4519 (1953); **78**, 2169 (1956).
4. A. F. Dokukina, M. M. Koton, O. K. Mineyeva, and V. A. Paribok, *Zhur. Fis. Khim.*, **30**, 109 (1956).
5. M. M. Koton, E. M. Moekvina, and F. S. Florinsky, *Zhur. Obshch. Khim.*, **21**, 1847 (1951); **22**, 789 (1952); *Zhur. Priklad. Khim.*, **26**, 660, 666 (1953); *Doklady Akad. Nauk S.S.S.R.*, **102**, 305 (1955).
6. M. M. Koton and T. M. Kiseleva, *Doklady Akad. Nauk S.S.S.R.*, **89**, 465 (1953).
7. G. B. Bachmann and D. D. Micucci, *J. Am. Chem. Soc.*, **70**, 2381 (1948).
8. K. Winterfeld and C. Heinen, *Ann.*, **573**, 85 (1951).
9. I. F. Andreeva, M. M. Koton, *Doklady Akad. Nauk S.S.S.R.*, **110**, 75 (1956).
10. W. Carothers and J. Williams, *J. Am. Chem. Soc.*, **53**, 4214 (1931).
11. A. N. Pravednikov and S. S. Medvedev, *Doklady Akad. Nauk S.S.S.R.*, **103**, 461 (1955); **106**, 579 (1956).
12. D. Elliott, *J. Am. Chem. Soc.*, **73**, 754 (1951).
13. G. B. Bachmann and L. Heisey, *J. Am. Chem. Soc.*, **70**, 2378 (1948).
14. R. Flowers and L. Flowers, *J. Am. Chem. Soc.*, **71**, 3102 (1949); *U.S. Pat.* 2,499,187; *Chem. Abstr.*, **44**, 5303 (1950).
15. M. M. Koton and O. K. Burnina, *Doklady Akad. Nauk S.S.S.R.*, **113**, 1063 (1957).

STAT

Synopsis

The polymerization of vinyl derivatives of naphthalene and of the heterocyclic series, containing the atoms of nitrogen, oxygen, and sulfur has been investigated. It is proved that an increase in the number of condensed rings in the radicals replacing the hydrogen atoms in the ethylene molecule, as well as the introduction of heteroatoms (nitrogen, oxygen, sulfur) into these radicals increase the polymerization ability of the above compounds.

Discussion

G. Hardy (Budapest): In our laboratory we have studied the reactivity of complicated vinyl esters in relation to the acid radical. In the course of this work the vinyl ester of furancarboxylic acid was synthesized. This monomer could not be polymerized either with radical-type initiators or with ionic-type catalysts. Thus it is interesting to compare the increase in reactivity of 2-vinyl furan with the nonpolymerizable vinyl furancarboxylate.

J. C. Bevington (Birmingham): Have the properties of these polymers been examined? The optical and photochemical properties might be particularly interesting.

M. M. Koton (Leningrad): We have also worked with furylacrylic acid and its esters and also noticed that they did not polymerize. In reply to Prof. Bevington's question: The polymers are transparent thermoplastic materials having various values of characteristic viscosity, softening temperatures, and dielectric properties.

K. J. Ivin (Leeds): Prof. Koton reports that vinyl decalidronaphthalene does not polymerize, even if heated for many hours at high temperature. I should like here to make the general point that an increase in temperature is generally unfavorable toward polymerization in the thermodynamic sense and that the rate of polymerization (for addition polymerization) will fall to zero at the temperature (the ceiling temperature T_c) at which the free energy of polymerization has fallen to zero (under the particular concentration conditions used in the experiment).

In the case of vinyl decalidronaphthalene, it is unlikely that it will polymerize by free radicals at low temperature even if thermodynamically possible (for reasons given by Prof. Smets in a comment following my paper). However, the above considerations should be borne in mind when testing a compound for polymerizability, and a wide range of temperatures, particularly below room temperature, should be tried.

M. M. Koton: I can say that we carried out the experiments over a wide temperature range and that we calculated the activation energy. There is a great difference here. For vinyl furan it is 17 kcal./mole, for vinyl dibenzofurans, 12 kcal./mole. Even this is an indication of the polymerization tendency, to say nothing of the circumstance that the experiments were carried out in a wide range of 0-100°, in the presence not only of radical but also ionic catalysts.

G. J. G. Smets (Louvain): Have some determinations been carried out concerning the kinetics of polymerization of vinyl decalin? Does this compound behave "normally" with respect to the concentration of the initiator, i.e., is the rate of polymerization proportional to the square root of the concentration of initiator?

M. M. Koton: We intended to elucidate why the vinyl derivatives of polynuclear hydrocarbons polymerize extraordinarily easily. Vinyl phenanthrene and vinyl anthracene cannot even be successfully isolated since they polymerize immediately during the dehydration of the corresponding carbinols. We therefore synthesized a series of hydrocarbons in which the vinyl group was conjugated with a larger or smaller number of double bonds. The polymerizations were carried out in a certain temperature range under the same conditions (without an initiator). I do not state that vinyl decalin does not polymerize, but only that under these conditions vinyl decalin did not show any sign of polymerization. Vinyl tetralin polymerized distinctly, and α - and β -vinyl naphthalenes particularly easily.

G. J. G. Smets: It is not correct to compare the polymerization rates if the kinetics of the polymerizations compared are not the same. In vinyl decalin there is an "allylic" hydrogen present and all the allylic monomers are different from the kinetic point of view, from, let us say, aromatic vinyl derivatives, (styrene, etc.).

A. L. Klebanik (Moscow): I agree with Prof. Smets that the reason for the decrease in the polymerization rate of vinyl decalin might be the presence of the active α -methylene hydrogen in this compound which is absent in aromatic derivatives.

O. F. Solomon (Budapest): I am not surprised by the polymerization tendency of the compounds investigated by Prof. Koton since we ourselves have carried out interesting experiments with vinyl furans. When comparing their polymerization with other heterocyclic vinyl derivatives we investigated also the polymerization of chlorovinyl furan. Whether the conjugated compounds can or cannot be polymerized catalytically was proved by me in 1954-56. Cyclooctatetraene which polymerizes by Na in liquid ammonia and yields a polymer of a similar molecular weight as vinyl furan and chlorovinyl furan,

STAT

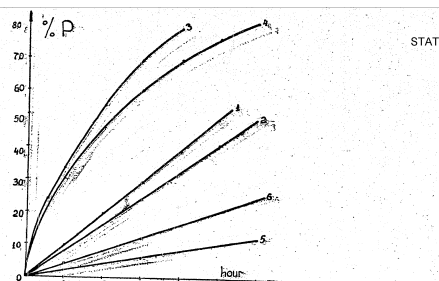


Fig. 1. The polymerization rate of vinyl derivatives of naphthalene. (1) 1-VN at 108°C . (2) 2-VN at 108°C . (3) 1-VN at 110°C . (4) 2-VN at 108°C . (5) 6-VT at 108°C .

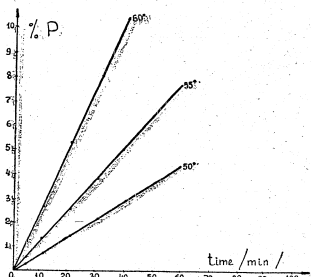


Fig. 2. The polymerization rate of 2-vinyl pyridine.

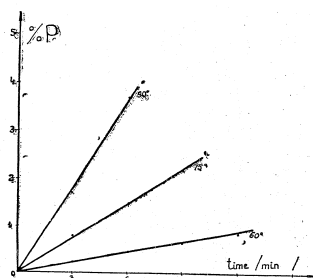


Fig. 3. The polymerization rate of 2-vinyl quinoline.

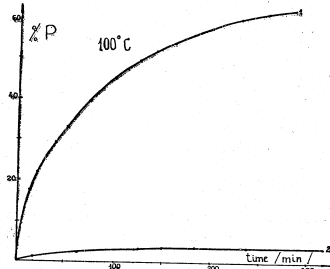


Fig. 4. The polymerization rate of vinyl derivatives of thiophene. (1) VDBT. (2) VT. 1 M solution in toluene, 0.5 mole-% peroxide.

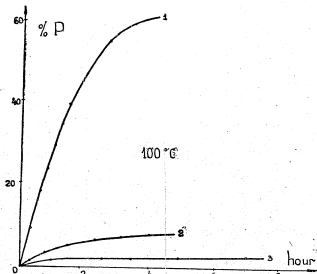
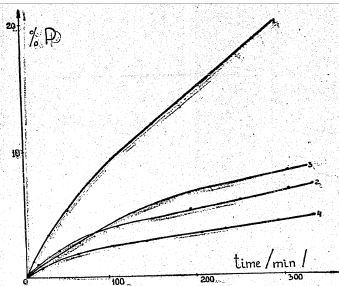


Fig. 5. The polymerization rate of vinyl derivatives of furan. (1) VDBF. (2) VBF. 1 M solution in toluene, 0.5 mole-% peroxide.



STAT

Fig. 6. The polymerization rate of 2-vinyl furan and 2-vinyl thiophene. (1) VT at 100°C. (2) VF at 100°C. (3) VT at 80°C. (4) VF at 80°C. 0.5 mole-% peroxide.

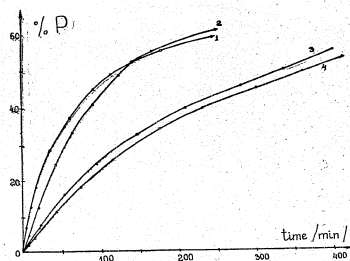
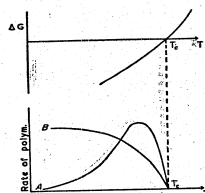


Fig. 7. Polymerization rate of 2-vinyl dibenzofuran and 2-vinyl benzothiophene. (1) VDBT at 100°C. (2) VDBF at 100°C. (3) VDBT at 80°C. (4) VDBF at 80°C. 0.5 mole-% peroxide; 1 M solution in toluene.



(A) Catalytic initiation. (B) Photochemical initiation.

Dielectric Losses and Polarization of Polymers

G. P. MIKHAILOV, *Institute of High-Molecular Compounds, U.S.S.R. Academy of Sciences, Leningrad, U.S.S.R.*

STAT

INTRODUCTION

Our report deals with two groups of experimental investigations of dielectric losses and polarization of amorphous polymers.

These investigations are very numerous and cover many polymers of different chemical composition. It is evident that in a short paper we can only mention some results of these investigations; *i.e.*, those which are necessary for an understanding and consecutive description of the studies in question.

The first group includes investigations which deal with the regularity of these properties of the polymers in a high-elastic state.

The second group includes our recent investigations made with the object (depending on their structure) of giving a certain relative assessment of those molecular interactions which determine the character of thermal motion in the polymers. In these investigations we used a method of effective dipole moment which in recent time has been considerably developed through new theories of dipole polarization which have established a more strict connection between dielectric permittivity and molecular values.

1. Dipole-Elastic Losses

The examination of the tangent of dielectric losses ($\tan \delta$) and dielectric permittivity (ϵ') of a series of amorphous polar polymers has shown that the dependence of the values on temperature and frequency bears a relaxation character.¹

These regularities are practically valid for all known polymers which are in a high-elastic state and are therefore called dipole elastic losses.²

Analysis of the data obtained by us and by a number of other investigations leads to a conclusion that dipole-elastic losses (further on this term will be abbreviated as " τ_{d-e} " losses) can be described by segmental motion of polymolecules.

The basis of our work was as follows:

(a) Relaxation time τ_{d-e} of losses found from the position of maximum $\tan \delta$ of temperature-frequency dependences is decreased³ when a polymer is plasticized by low molecular compounds. This means that the region $\tan \delta_{\max}$ is shifted toward lower temperatures.

(b) τ_{d-e} is decreased as the chain length of the side radical of a macro-chain grows due to the incorporation of non-polar groups (homologous series of polyvinyl alcohol acetals, esters of methacrylic acid, etc.).⁴

(c) τ_{d-e} of copolymers, polar with non-polar monomers, is determined by the concentration of the components while the value of losses in the $\tan \delta$ area is proportional to the concentration of the polar component.⁵

2. A Study of Dipole Polarization of Polymers in a High-Elastic State and in a Solution of a Non-Polar Liquid

Our investigations of dipole moments of elementary chain units of macromolecules of some vinyl polymers and of polymers of a homologous series of methacrylic acid esters have shown that in determining these moments in a high-elastic state or in a solution of non-polar solvent, only their effective values μ_{eff} can be found.⁶

The modern theories of dipole polarization of a liquid consider μ_{eff} to be the value of a molecule dipole moment consisting both of the moment resulting from the molecule structure and of its change caused by the molecular long and short range interaction.⁷

Owing to the chain structure of macromolecules, two kinds of dipole molecular interaction can be distinguished in polymers: intermolecular and intramolecular. The first can probably be attenuated when dipole polarization of molecules is studied in a solution, while the second can remain and its analysis requires an investigation of this polarization in special systems, for example, in copolymers of polar monomer with non-polar ones.

Table I contains the results of investigation of these molecular interactions by method of effective dipole moments. These results were obtained in our laboratory.

TABLE I

Name	μ_0 (in Debyes)	μ_{eff}/μ		Polymer in a high- elastic state
		Monomer in a solution	Polymer in a solution	
Methyl acrylate	1.75	0.96	0.76	0.78
Methyl methacrylate	1.78	0.98	0.74	0.76
Ethyl methacrylate	1.85	0.95	0.73	0.79
Propyl methacrylate	1.89	0.96	0.75	0.77
Butyl methacrylate	1.88	0.94	0.74	0.77
Phenyl methacrylate	1.75	0.91	0.74	—
Dichlorophenyl methacrylate	2.34	0.92	0.62	—
Panchlorophenyl methacrylate	2.73	0.91	0.59	—

The second column of Table I gives the dipole moments μ_0 of the molecules of hydrogenated monomers determined and calculated by the method for Debye polar solutions or, in other words, μ_0 is the moment of a free molecule.

Columns 3, 4, and 5 give the values of μ_{eff}/μ which are relative measures of the molecular interactions, where μ is the dipole moment of a molecule or of a monomer link of a polymolecule calculated from the well-known Onsager formula:

$$\mu = \frac{n^2 + 2}{3} \frac{2\epsilon + n^2}{2\epsilon + 1} \mu_0$$

It is evident from Table I that in the case of a monomer in a solution extrapolated to an infinitely small concentration of a polar component, ($\mu_{eff}/\mu \rightarrow 1$, *i.e.*, no molecular interaction of dipole character takes place.

For a polymer with the same extrapolation in a high-elastic state, ($\mu_{eff}/\mu < 1$, and is less the larger μ_0). Hence we conclude that the intramolecular interaction between polar groups of the chain in the given polymers remains because of the chemical bonds linking these groups together, and that it exists because of the polar groups and therefore grows as μ_0 is increased.

STAT

STAT

TABLE II

Monomer in a solution	Weight in %	Copolymers of methylmethacrylate with Styrene				Polymer in a solution
		24.0	40.5	55.5	80.5	
μ_{eff}/μ	0.96	0.98	0.88	0.83	0.72	0.75

Table II gives the results of μ_{eff}/μ for a copolymer of methyl methacrylate with styrene, the latter being considered to be non-polar. These data show that up to 24% concentration of methyl methacrylate in the copolymer μ_{eff}/μ has the same value as for a monomer in a solution (Table I). As the percentage of methyl methacrylate in the copolymer is increased, μ_{eff}/μ is decreased and at 80.5% reaches the value which is observed for a solution and for a high elastic state of a polymer, i.e., at up to 24% concentration of methyl methacrylate these copolymers, by the character of molecular interactions, are equivalent to polar solutions and consequently the distribution of monomeric links of methyl methacrylate and styrene is statistical.

3. Dipole Radical Losses

In certain polar amorphous polymers in a glassy state, relaxation dielectric losses are observed. By the character of their regularities $\tan \delta$, these losses can be called dipole-radical losses (further on this term will be abbreviated as $d-r$ losses). This name was given to the phenomenon because $d-r$ losses reflect thermal motion in the polymer (depending on structure) either of individual links of macromolecules or of polar radicals. The number of works devoted to investigation of these losses is considerably less than the number of those dealing with $d-e$ losses.

At the same time, the dependences $\tan \delta$ of $d-r$ losses do not have this community for polymers of different chemical structure which is observed for $d-e$ losses.

Of the regularities grounding the supposed mechanism of $d-r$ losses, the following data can be cited. These data were obtained in the investigations of polymers of vinyl acetate, methyl acrylate, methyl vinyl ketone, vinyl chloride, polyvinyl ester acetals, and cellulose esters.

(a) The temperature dependence of relaxation time satisfies the following equation

$$\tau_{d-r} = \tau_0 e^{U/RT} \quad (1)$$

where τ_0 lies between 10^{-12} and 10^{-14} sec, and U , the energy of activation, has values from 6 to 11 kcal./mole. The numerical values of τ_0 and U are in agreement with the conceptions developed in Debye's theory of dipole polarization of polar liquids.

This process can be represented as an elementary act of dipole turn overcoming the potential barrier which is determined by the energy of molecular interaction forces.

(b) The position of the region $\tan \delta_{max}$ on the temperature or frequency curves of $d-r$ losses does not depend on the concentration of the components in the copolymers of methyl vinyl ketone with styrene and of methyl acrylate with styrene. This means that τ_{d-r} is independent of the concentration of the components, while the value of $\tan \delta_{max}$ grows linearly as the concentration of polar component is increased.

4. Investigation of Molecular Interaction by μ_{eff} -Method According to Dipole-Radical Values of $\tan \delta$ and ϵ' of Certain Polyesters of methacrylic Acid*

Figure 1 shows the dependence of $\tan \delta$ and ϵ' on the temperature at frequencies of 20 and 100 cycles per second for the polymers PMMA, PEMA, PPMA, PBMA, and P-iso-PMA.*

* PMMA is the abbreviation of polymethyl methacrylate and correspondingly of other homologues such as ethyl, propyl, etc.

From Figure 1 it is evident that for each PMMA $\tan \delta$ curve and for curve 1 for PEMA two temperatures are observed at which $\tan \delta$ passes through a maximum. One of the regions of $\tan \delta_{max}$ for PMMA which lies within the interval of temperatures below 110°C . (this is the temperature of PMMA transition to solid state, or T_g) corresponds to $d-r$ losses, while the second region of $\tan \delta_{max}$ is at a higher temperature than T_g and is related to $d-e$ losses. On the right-hand side of Figure 1 there are curves of $\epsilon' = \varphi(\epsilon)$; here also changes for two regions of $\epsilon' = \varphi(\epsilon')$ (Fig. 1) are observed.

A more detailed study of $\tan \delta = \varphi(T)$ (Fig. 1) shows that the larger the number of homologue, the regions of $\tan \delta_{max}$ of $d-e$ losses are displaced toward low temperatures, while the second region corresponding to $d-r$ losses is not displaced. The latter leads to a disturbance of the symmetry of $\tan \delta = \delta(T)$ curves.

In the case of the same curves for P-iso-PMA, again we have a division of $\tan \delta$ regions because the region of $d-e$ losses is displaced toward higher temperatures, while the region of $d-r$ losses, on the contrary, is displaced toward low temperatures. Figures 2 and 3 shows frequency functions of $\tan \delta$ for some temperatures covering both the solid and high-elastic states of PMMA and P-iso-PMA. On the curves of $\tan \delta = \varphi(f)$, Figures 2 and 3, the positions of two $\tan \delta_{max}$ regions can also be seen, and therefore these curves are asymmetric.

For polymers EMA, PMA, and BMA, the curves $\tan \delta = \varphi(f)$ are analogous and therefore are not shown.

Figure 4 shows $\log f_m$ as a function of $10^3/T$, where f_m is the frequency of relaxation and T the absolute temperature of the region of $d-r$ losses maximum. From Figure 4 it is evident that this data for normal polymer homologues fall approximately on curve 1, while for P-iso-PMA they fall on curve 2. From this data we conclude that, first, relaxation time of τ_{d-r} losses for all investigated normal polymer homologues has the same value, i.e., is independent of the number of CH_2 groups, and, second, the exponential function (1) is satisfied.

At the same time the energy of activation for these polymers has a larger value of 21 kcal./mole, i.e., a certain specific feature is peculiar to the process of relaxation on these polymers.

By the temperature interval, the curves 1 and 2 cover both the solid and high-elastic state. Therefore $d-r$ losses actually reflect a definite character of thermal motion which is peculiar to polymolecules of a given structure and is independent of the state of the polymer. The energy of activation U for P-iso-PMA calculated from curve 2 (Fig. 4) is equal to 16 kcal./mole, i.e., is less than for normal polymer homologues. This decrease in U can be explained by looser packing of an iso-compound of the polymer. For the purposes of a more detailed analysis of the data obtained, we used the method of arched diagrams on a complex plane of ϵ' and ϵ'' values to find equilibrium dielectric permittivities ϵ_0 and ϵ_∞ for $d-r$ losses.¹

From the values of ϵ_0 and ϵ_∞ , molecular weight M of the monomer link, and polymer density ρ , it is possible to calculate μ_{eff} values, using the following formula:

$$\mu_{eff} = 7.36 \times 10^{-21} \sqrt{\frac{TM}{\rho} \frac{(2\epsilon_0 + 1)(\epsilon_0 - \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)}} \quad (2)$$

STAT

Figure 5 shows the results of calculations of μ_{eff} from formula (2). From this it is evident that in a solid state the value of μ_{eff} is largest for PMMA and the smallest for P-iso-PMMA.

Within the temperature interval of T_g , μ_{eff} sharply increases and reaches a value which is independent of temperature and corresponds to the value of μ_{eff} determined by other methods. Because of the position of d-e losses, it was impossible to determine d-r losses for PBMA. However, the lower value of μ_{eff} for some polymers in a solid state (Fig. 5) can be explained by the fact that the dipole orientation is strongly hindered by the chain, i.e., the dipole (for our polymers C=O) is strongly correlated due to the intensive intermolecular interaction of macromolecules.

It is also interesting to note that for PMMA this correlation is smallest, because the value of $\tan \delta$ is largest in the region of maximum d-r losses and correspondingly the largest values of μ_{eff} have been found.

CONCLUSION

The data obtained in this work on dielectric losses and polarization for some polymers of the esters of methacrylic acid make it possible to assume that a determining character of thermal motion in the polymers in a high elastic state is the intramolecular interaction and in a solid state the intermolecular one.

References

1. Michailov, G. P., *Uspekhi Khim.*, **24**, 875 (1955). Kobeko, P. P., *Amorphous Substances*, Academy of Sciences, U.S.S.R., 1962. Kobeko, P. P., Michailov, G. P., and Novikova, Z. T., *Zhur. Tekh. Fiz.*, **14**, 24 (1944).
2. Michailov, G. P., *Zhur. Tekh. Fiz.*, **11**, 1395 (1951).
3. Fuoss, R. M., *J. Am. Chem. Soc.*, **63**, 2140 (1941). Davies, J., Miller, R., and Ruse, V., *J. Am. Chem. Soc.*, **63**, 361 (1941). Dyson, A., *J. Polymer Sci.*, **7**, 133, 147 (1953). Hoff, E. A., Robinson, D. W., and Willbourn, A. H., *J. Polymer Sci.*, **18**, 161 (1955). Deutsch, K., Hoff, E. A., and Reddish, W., *J. Polymer Sci.*, **13**, 565 (1954).
4. Erlich, T. M., and Tcherbak, P. N., *Zhur. Tekh. Fiz.*, **25**, 9 (1955). Funt, B., and Suterland, *Can. J. Chem.*, **30**, N2, N125 (1952). Kobeko, P. P., and Kuntchitska, N. M., *Zhur. Tekh. Fiz.*, Special Number, Academy of Sciences, U.S.S.R., 1958.
5. Michailov, G. P., and Krasner, L. V., *Zhur. Tekh. Fiz.*, **25**, 1758 (1955).
6. Burstein, L. L., and Michailov, G. P., *Zhur. Tekh. Fiz.*, **27**, 688, 694 (1957).
7. Harris, F., and Alder, B., *J. Chem. Phys.*, **21**, 6 (1953). Frolich, H., *The Theory of Dielectrics*, Oxford, 1949.
8. Borisova, T. I., and Michailov, G. P., *Zhur. Tekh. Fiz.*, in press.
9. Cole, R. H., and Davidson, D. W., *J. Chem. Soc.*, 1952, 9, 20.

Synopsis

Results of research on the dielectric losses and polarization of polymers are presented. In the first and second parts of the paper these behaviors of the polymers are considered for high-elastic state. The dielectric losses are shown to be of relaxation character since they can be described by the segmental thermal motion of polymolecules. The second part deals with effective dipole moments of elementary chain units of macromolecules of the homologous series of methacrylic acid esters. It is stated that for the polymers under consideration the intramolecular interaction is of considerable significance. The third part of the report supplies data on the dielectric losses and polarization research of the same polymers in the glassy state. In this case the losses of relaxation character, called dipole-radical, are observed, as they can be described by the thermal motion of separate polar groups or radicals. The application of the method of effective dipole moments for analysis of the experimental data has brought us to the conclusion that it is the intermolecular interaction which is of greater importance for the dipole-radical losses.

Discussion

L. de Brouckère (Bruxelles): It is extremely encouraging to see that difficult experimental work carried out quite independently in Leningrad and in Brussels leads to very similar results notwithstanding minor discrepancies in the numerical data.

I would like to ask Prof. Michailov if the values of ϵ_{∞} deduced from the "rainbow diagram"—i.e., the Cole and Cole method—were equal to the square of the refractive index, and if ϵ_{∞} was really the static dielectric constant. If this was not the case, equation (2) of Professor Michailov's paper cannot be used for the evaluation of an effective dipole moment.

I would also like to know if the measurements on polyisopropyl methacrylate were carried out above or below T_g .
G. P. Michailov (Leningrad): The values of ϵ_{∞} for PMMA and a number of other investigated polymers of a given homologous series were several per cent higher than the square of the optical index of refraction.

ϵ_0 and ϵ_{∞} were determined by the method of circular diagrams on the complex surface of the quantities ϵ' and ϵ'' . These data were used in evaluation of μ_{eff} below and above T_g . The values of μ_{eff} found above T_g were (within limits of accuracy of the determination) approaching the values of μ_{eff} found according to the method of polar solutions.

The softening temperature T_g of the *p*-iso-form (polyisopropyl methacrylate) is approximately 100°C., according to dielectric measurements. This can immediately be seen from the curve for $\tan \delta = \varphi(\delta)$, found on measurements with a frequency of 15 cycles per second.

STAT

STAT

STAT

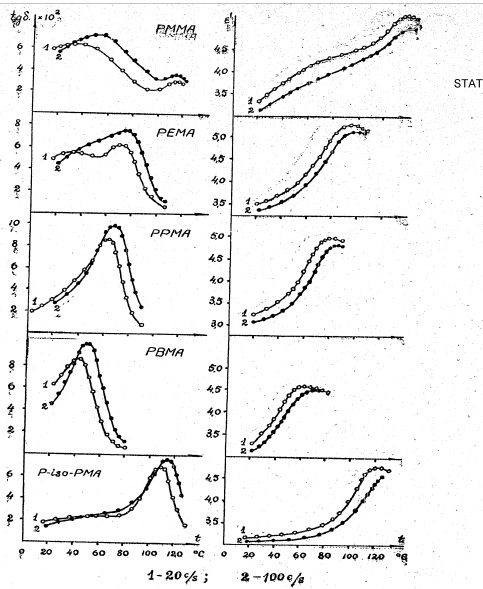


Figure 1.

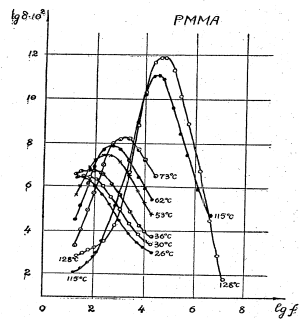


Figure 2.

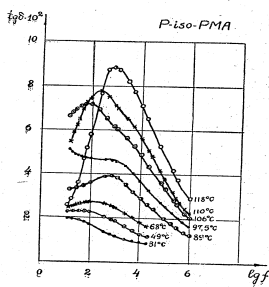


Figure 3.

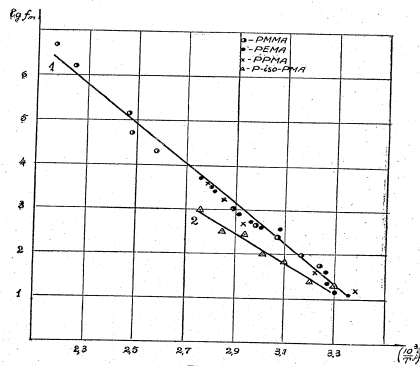


Figure 4.

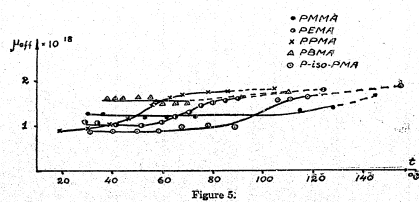
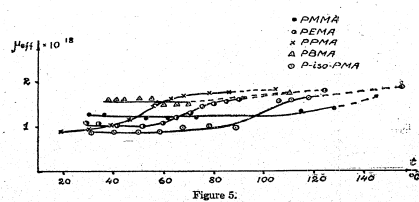
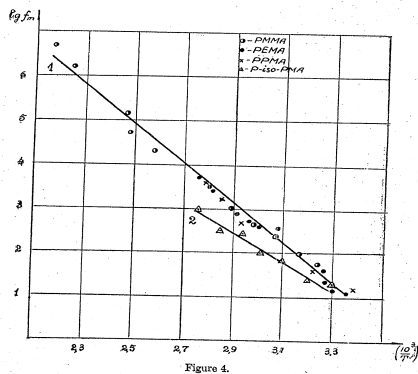
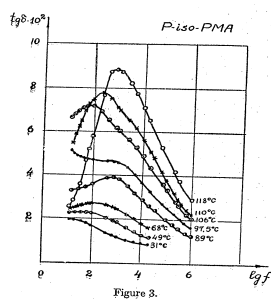
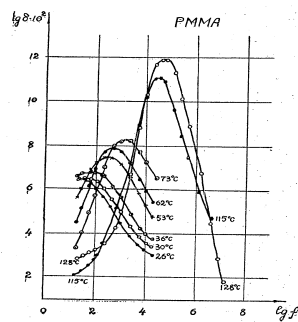
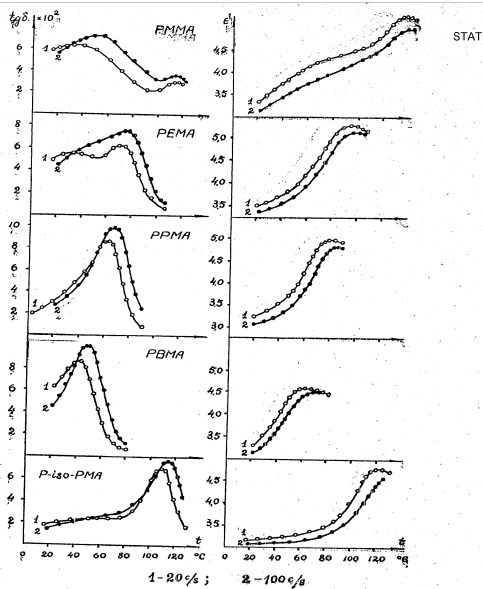


Figure 5.



STAT

Structure and Phase State of Polymers

V. A. KARGIN, *Karpov Institute for Physical Chemistry, Moscow, U.S.S.R.*

STAT

The aim of each structural investigation is to determine the spacing both of the molecules of the substance under investigation and of the atomic and molecular groups of which it consists. For linear polymers, ordinary structural methods are applicable for determining the spacing of individual molecular groups but they give very little information about the spacing of large molecules. Therefore our judgments of the mutual distribution of macromolecules are based on comparing data received by a number of techniques, especially electron microscopy. In my report I shall deal precisely with the structures due to the mutual distribution of macromolecules and the relations which exist between the formation of these structures and the phase transformations taking place in polymers.

The flexible chain molecules can either coil into balls, forming globular structures, or assume a completely irregular chaotic pattern, becoming interwoven with each other, or they can gradually acquire a certain order, taking up a more or less parallel position. It may be supposed, with a great deal of certainty, that the principal source of this order appearing in the system of many polymer chains is their mutual orientation. This mutual orientation of chains may be caused by intermolecular interaction (resulting at most in crystallization), by an orientation arising from constraints exerted and particularly from the flow of polymers due to mechanical strain applied to the polymers and—in case of natural polymers—by an orientation resulting from the morphological conditions of the polymer formation. Thus, high order in polymers may be achieved in different ways. Here the problem of the concepts of the orientation and crystallinity of the polymer naturally arises. If we stretch a linear polymer, its chain molecules will orient in the direction of the stretching, and consequently with regard to each other. In the process the chains will be arranged in an increasingly regular order, and thus it is possible to obtain extremely well-ordered fibers, which gave an abundant interference pattern very similar to that of well-oriented and polycrystalline substances. Is such a highly oriented polymer crystalline? Can the phase transformations be regarded as a basic source giving rise to high order in polymers? How can the phase state of such an oriented polymer be determined? It seems to me that these problems can be considered most thoroughly by taking cellulose as an example.

STAT

Cellulose is a well-ordered polymer which gives a comparatively rich interference pattern. Most workers consider it a crystalline polymer, containing both crystalline and amorphous regions. Yet it is possible to prove in several ways the absence of crystallinity of cellulose even when it is very highly oriented.

Electron diffraction investigation of cellulose and its ethers¹ reveals that they are amorphous and that the entire electron diffraction diagram is determined by the ordered arrangement of atoms in the molecules of cellulose, and this gives evidence as to the absence of strict order in the mutual distribution of these molecules.

The amorphous state of the isotropic cellulose films was in itself no proof of the amorphous structure of oriented fibers, for crystallinity could have resulted in stretching cellulose just as is the case in the stretching of natural rubber. To determine this, a simple method suggested by Katz was used.

During the X-ray investigation the oriented sample under investigation was rotated around the axis coinciding with the direction of the X-ray. This resulted in a diagram showing, instead of texture, a system of rings analogous to those which appear in the electron diffraction record of an isotropic sample. Comparing the pictures received for initial isotropic cellulose and for highly oriented fibers, we can see that there is no new interference taking place in the process of orientation, and no phase transformations.

These data were recently confirmed by Mikhailov and Fainberg² who determined the solubility heats of isotropic and oriented cellulose in quaternary ammonium bases and found that they differed very little, 1 to 1.5 cal./g., a fact which testifies to the absence of phase transformations of the first type in cellulose orientation.

Thus the example of cellulose convinces us that high order in a polymer may not be attained only by crystallization. In this case the geometrical order will only be connected with the regular structure of chain molecules and their parallel distribution along the orientation axis, any shifts in the chains both in the direction of orientation and azimuthally being possible.

The mutual orientation and ordering of chains in polymers may take place both under the influence of outside forces (formation of oriented fibers) and as a result of intermolecular interaction, leading to the formation of clusters in the manner which occurs in liquids. It may be supposed that these clusters are large and well ordered, particularly in case of rigid chains.

This suggests that crystallization is preceded by ordering processes taking place in an amorphous polymer. This can be verified in two ways: by a comparative structural investigation of the crystallizing polymers at temperatures below and above the melting points of their crystals, and by a similar investigation of oriented polymers, the only difference being that the orientation of the polymer remains unchanged during melting and crystallization.

Recently Ermolina and Markova³ carried out an electron diffraction study of polyethylene terephthalate and polychlorotrifluoroethylene at temperatures above and below the melting points of their crystals. The results turned out to have many features in common.

Figures 1 and 2 show curves indicating the distribution of the intensity of coherent angle scattering for the two polymers both in crystalline and amorphous states. These curves have been obtained from an electronogram taken at different exposures and normalized according to the curves of atomized factors computed for the repeated atomic groups of the polymers, making an allowance for noncoherent scattering. The coincidence of basic maxima of the electron diffraction curves by crystalline and molten polymers becomes immediately manifest.

These data were used for evaluation of the order existing in amorphous polymers by the radial distribution method, usually applied for the determination of the structure of amorphous bodies, but recently used for polymers too.⁴ In plotting the curves of radial distribution, six maxima were found for polychlorotrifluoroethylene and four for polyethyleneterephthalate. All the former maxima correspond to the distances between atoms in the molecules of polymers, and only for cases with orderly structure of chains. The latter intensive maxima, which are 5.2 Å. for polychlorotrifluoroethylene and 4.45 Å. for polyethyleneterephthalate, are determined by the mutual distribution of the polymer molecules. The same distances prevail for crystalline states too.

Thus we can see from the two polymer investigations that a considerable part of the interference pattern is due to intramolecular scattering, which in its turn is caused by the orderly structure of polymer chains. We can also see that the ordering in the mutual distribution of chains can be traced to the amorphous structure. Such ordering phenomena have been widely known for liquids ever since the first works of Stewart. The formation in polymers of well-ordered clusters with their large and asymmetrical molecules is in harmony with the most general conceptions of the structure of liquids, and the preservation of crystalline nuclei was found in molten polymers as well.

It is much more difficult to carry out an experiment for the comparative structural study of well-oriented polymers which are either in an amorphous or crystalline state but possess an equal degree of orientation. To do so it is necessary to prevent the flow of the polymers at high temperatures by creating a structural framework which is not dense but sufficiently stable, to orient the polymer at a relatively low temperature at which the high tensile strength makes it possible to apply greater strain to the polymer, to fix the ends of the stretched sample, and to heat it to a temperature higher than the melting point of the crystals. The principal difficulty of such an experiment is that while being heated the sample ruptures owing to the stresses that come into being in it. This difficulty was overcome by Markovskaya who placed a strongly oriented thread into a thin walled capillary tube which prevented the contraction of the thread during subsequent heating. Thus it was possible to investigate by the x-ray technique polytetrafluoroethylene and polyethylene (weakly irradiated by high-speed electrons) and to eliminate the flow in the form of oriented threads, the experiments being carried out at the temperatures corresponding to the crystalline and to the molten states. Figures 3 and 4 show photographs of these polymers, which again reveal the great resemblance between oriented amorphous and crystalline polymers. In this way it is possible to divide the interference pattern of an oriented crystalline polymer, and to find out which part of this pattern is due to the mere uniaxial orientation of regularly formed chains and which to the appearance of a stricter order in the course of crystallization.

STAT

The general conclusion to be drawn from this part of my report is that polymers may be well ordered in an amorphous state too, and that this ordering is a necessary though insufficient condition for subsequent crystallization.

The structural methods give but an indirect possibility of elucidating the mutual distribution of the large molecules. So far electron microscopy is the only method for direct observation of polymer molecules. To determine the mutual distribution of molecules in polymers and find the nature of the crystalline regions a number of attempts has been undertaken, of which I am now reporting.

In the investigation of crystalline polymers with electronic microscope, complex formations are usually found which penetrate the entire mass of the polymers and are called spherulites. Usually these formations are regarded as aggregates of elementary crystals. It could be expected that by destroying the crystals of a polymer we should also destroy the spherulites. On the contrary, if we could destroy the spherulites, preserving the crystallinity of the polymer, we would be able to observe the crystal regions in polymers. We carried out such experiments with Koretskaya.

It is a matter of common knowledge that the irradiation of polyethylene and polyamides by high-speed electrons reduces them to an amorphous state. Samples of polyethylene and the copolymer of caprolactam with hexamethylenediamine and adipic acid display a high degree of crystallinity when examined by the electron microscope and electron diffraction techniques and readily form spherulites. After the irradiation of thin films of these polymers they become amorphous, but the spherulites remain quite unchanged. Figure 5 shows the photographs of the same samples, first recorded by means of electron microscopy and electron diffraction, and then photographed after electron bombardment. The electronograms of the samples show their complete amorphousness, and we can see that the disappearance of crystallinity is not accompanied by the destruction of spherulites.

STAT

Evidently, the fibrous structure of the spherulites is not caused by an accumulation of crystallites, but by the mutual distribution of chains, characteristic of the formation of crystalline structures. It is of interest to note that heating up to the temperatures corresponding to the softening of these irradiated films does not result in any changes in the electron microscopic pattern either, and we again can be fairly convinced of the high degree of order which may be observed both in the crystalline and in the amorphous states of the polymer.

When thin films of polyethylene are stretched, the spherulites are destroyed, but the polymer preserves a high degree of crystallinity. Figure 6 shows an electron microscopic photograph of a stretched polyethylene film (direct enlargement, 15,000). The neck formation is clearly seen, a phenomenon whose appearance is connected with structural processes, and not with macro-phenomena as is sometimes supposed. The stretching process is accompanied by the destruction of spherulites and the division of the sample into a system of thin threads. Although spherulites are absent, no formations bearing distinct resemblance to crystals are to be observed. The only thing to be observed is a certain unevenness in the threads, which becomes clearly visible by dusting the samples with chromium or palladium. Figure 6 shows some sections of the threads in which these formations are clearly to be seen. It is possible that these irregularities in the threads are nothing but the elementary crystalline formations of whose presence we can so confidently judge when using the ordinary structural methods.

Thus we can see that the destruction of crystallites does not lead to the disappearance of spherulites, and that the destruction of spherulites does not reduce the crystallinity of the polymer. It is natural to suppose that the spherulites are not aggregates of crystals, but the result of the ordering of chains accompanying crystallization.

It is very interesting to note that the ordered bundles of chain molecules are to be easily observed both in spherulites and in stretching polymer films, while the crystalline regions themselves almost defy observation. A number of readily crystallizable polymers, of which gutta-percha is the most characteristic one, often yield undoubtedly crystalline films which prove completely blank when examined with an electron microscope. As for the oriented films of crystalline polymers, they can be seen in the photographs to be easily divided into fine threads. Small thickenings are to be observed in these threads, and in certain places the entire thread seems to consist of small particles divided by thinner sections. Probably these irregularities are nothing else than elementary crystals, and at any rate the size of the elementary crystals cannot exceed the size of these irregularities.

The formation of thin threads can sometimes be observed in amorphous polymers, too. For instance, in tearing a thin film of polystyrene, fine threads may be observed on the spot of the rupture (Fig. 7). Similar pictures were obtained in the ruptures of polydichlorostyrene films. It is difficult to assume that such threads can be formed of polymers in which the chains are in complete disorder, and it seems to me that the appearance of such threads is also a sign of the presence of chain ordering in the initial polymer.

One more approach is possible in order to determine the arrangement of chains in polymers. When strongly diluted solutions of polymers are evaporated on supports of the substance, it is possible to observe individual molecules of the polymers with an electron microscope. An increase in the concentration of the solution makes it possible to observe the formation of aggregates of these molecules. In these studies carried out by Bakayev⁸ polyacrylic acid and its salts were taken as objects because here the shape of the chain molecules can be easily changed. Pure polyacrylic acid and its barium salt yield typical pictures of molecules coiled into peculiar spheric globules (see Figs. 8a and 8b). It is of interest to note that in the formation of aggregates, coiled chains do not mutually penetrate into each other. The photographs clearly show that the accumulations of molecules consist of individual spherical molecules.

A completely different picture is to be observed in the study of the salts of acrylic acid with strong bases univalent cations. In Figures 8c and 8d we see photographs of polyacrylates of sodium and cesium. We see that in this case threadlike structures appear, which seem to be the result of the aggregation of uncoiled stretched molecular chains. These studies were carried out with solutions with pH = 6.5, which corresponds to the maximum of viscosity and the greatest asymmetry of chain molecules.

Thus we can see that the stretched molecules of the polymers gather into bundles of more or less parallel chains. The cross section of these bundles or fibrils ranges in our experiments from 40 to 120 Å. for various salts, which is equivalent to the number of five to thirteen chains in a bundle. Completely analogous pictures are obtained for the salts of polyacrylic ethers of cellulose soluble in water. In all these cases it is possible to observe—proceeding from the diluted solutions in which all molecules are known to be far apart—how aggregates are formed out of the individual molecules, and how the structure of these aggregates is connected with the form of asymmetry of the polymer molecules. In the transition to linear forms, ordered groups of molecules appear, consisting of mutually oriented chains. These formations are undoubtedly amorphous and the examples given make it possible to see clearly what a variety of structures exists within the limits of the amorphous state and to come to the conclusion that the phenomena of the mutual ordering of chains are not in all cases connected with the phase transformations of a polymer.

Amorphous and crystalline polymers undoubtedly exist, and the extreme representatives of these groups are widely different in their properties. At the same time it is difficult to find properties which the representatives of both groups do not possess. For instance, crystalline polymers often display highly elastic deformation, while amorphous polymers are deformed with the development of a neck similarly to crystalline polymers. Studying the sorption capacity, it is sometimes impossible to find any difference between crystalline and amorphous states of polymers, etc. One may say that the difference between these states in polymers is much less pronounced than in the analogous low molecular substances. Usually attention is paid to the peculiarities in the structure of the crystals of polymers. In the present report I wished to draw some attention to the structure of amorphous polymers and to those phenomena of their chain ordering which can take place without phase transformations. The conclusion may be drawn that, while the crystalline polymers differ from the ordinary crystals by a lesser degree of order, it is by the high degree of order in their molecules that the amorphous polymers differ from low molecular liquids and from amorphous bodies. The presence of long molecular chains prevents the growth of crystals and favors the formation of well-ordered clusters and oriented structures, and this is the reason for relating the properties of these systems.

The appearance of well-ordered amorphous systems often leads to a misunderstanding based on the fact that amorphous polymers (or amorphous regions) are considered to be a system of chains irregularly interwoven, and the crystallization of the polymers is meant to be the only source for the introduction of order. This results in looking upon any ordered polymer as a mixture of a crystalline and an amorphous part, regardless of whether the ordering is connected with crystallization or not.

The view that cellulose is a crystallized polymer may be given as an example of this attitude.

A number of facts testify to the mutual ordering of the chains of linear polymers. It is possible that this ordering is a necessary though insufficient condition for crystallization. In fact, it is very difficult to imagine rapid formation of any ordered structures or crystals in a system of chains interwoven without any semblance of order. Such a process can only take place at a relatively slow rate as is the case, for instance, in the crystallization of unstretched rubber. But when crystallization proceeds at a rapid rate, and the melting temperatures of the crystals vary over a very narrow range,⁹ this means that no considerable displacement of long sections of the chains occurs in the process.

This, in its turn, means that a certain order in their distribution has been reached before crystallization. Polymers crystallizing at a rapid rate should be those with highest order in their amorphous state.

Though the crystallites of polymers form within the limits of bundles of mutually oriented chains or fibrils, there is no reason for considering these formations identical. The question of the geometrical forms of the crystalline areas is not yet clear and will become the object for future studies.

References

1. V. Kargin, V. Karpov, and Z. Pinsker, *Acta Phys. Chem. U.S.S.R.*, **7**, 646 (1957).
2. V. Kargin and D. Leipunskaja, *Zhur. Fiz. Khim.*, **14**, 312 (1940), **15**, 1011 (1941).
3. Kakinoki, *Proc. Phys. Math. Soc. Japan*, **21**, 95 (1939).
4. N. Mikhailov and E. Fainberg, *Doklady Acad. Nauk U.S.S.R.*, **109**, 1160 (1956).
5. A. Ermolina, G. Markova, and V. Kargin, "Study of structural changes in polyethyleneisphthalate and polychlorotrifluoroethylene over a range of melting temperatures of crystals," *All-Union Symposium on Electronography*, Moscow, March 1957.
6. A. Bjørnhaug, Ø. Eldefsen, and B. Tønnesen, *J. Polymer Sci.*, **12**, 621, (1954).
7. B. Weinstein, *Crystallography, U.S.S.R.*, **2**, 29 (1957).
8. A. Keller, *Proc. Roy. Soc. (London)* **A241**, 1, (1956).
9. V. Kargin and G. Markova, "Investigation of ordering in polymers due to crystallization and orientation," *Ninth All-Union Conference on the General Problems of Chemistry and Physics of High Polymers*, Moscow, January 1957.
10. V. Kargin and T. Koretskaja, *Doklady Acad. Nauk U.S.S.R.*, **110**, 1015 (1957).
11. V. Kargin and N. Bakayev, *Kolloid Zhur.*, **19**, 133 (1957).
12. L. Mandelkern, *Chem. Revs.*, **56**, 903 (1956).

Synopsis

In order to determine the structure and phase state of polymers and to define the spacing of molecular groups or atoms of which molecules of the substance under investigation consist, it is necessary to estimate the mutual distribution of macromolecules. The results of a number of investigations carried out by the electron microscope and by direct structural techniques make it a possibility of obtaining such an estimation. In this work the formation of ordered structures in amorphous polymers has been found by investigating solutions of polymers with the electron microscope. The study of thin oriented films of polymers by the above method confirms the possibility of mutual distribution of amorphous polymer chains and of crystallizable polymer chains after destroying the crystals. In investigating thin films of crystallizable polymers by the x-ray and the electron diffraction techniques at temperatures above and below the crystallization temperatures, a high degree of ordering has been found for the amorphous state of these polymers, too. From the data obtained, the conclusion is to be drawn that a fair mutual ordering of chain molecules can arise even in the amorphous state of polymers. Crystallization of polymers is but the last step in the process of mutual ordering of chain molecules.

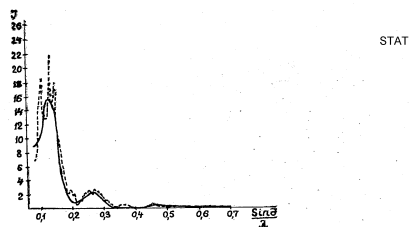


Fig. 1. The experimental intensity curves of electron scattering for polychlorotrifluoroethylene in crystalline (dashed line) and amorphous states (solid line).

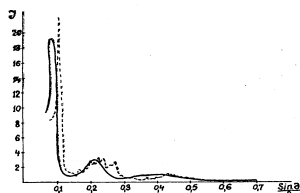


Fig. 2. The experimental intensity curves of electron scattering for polyethyleneterephthalate in crystalline (dashed line) and amorphous states (solid line).

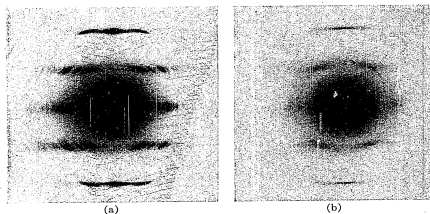


Fig. 3. Electron diffraction patterns. (a) Crystalline polyethylene film fully drawn. (b) Polyethylene film fully drawn after destruction of crystalline regions.

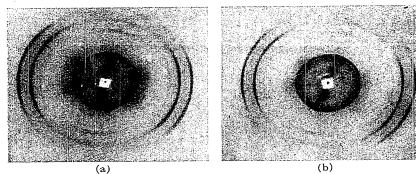


Fig. 4. X-ray diffraction patterns. (a) Crystalline polytetrafluoroethylene film fully drawn at 20°C. (b) Polytetrafluoroethylene film fully drawn at 390°C.

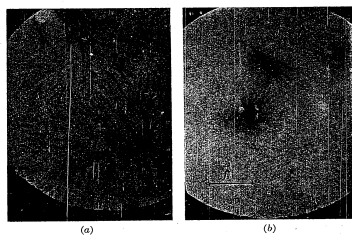
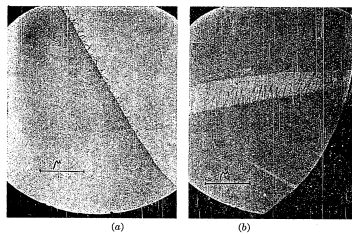


Fig. 5. Electron micrographs. (a) Polyethylene unstretched film 16,000X. (b) Polyamide (copolymer ε-caprolactam hexamethylenediamine and adipic acid) cast from ethyl alcohol supported on nitrocellulose. 12,000X.



Fig. 6. Electron micrograph of polyethylene film fully drawn (chromium shadowed) 15,000X.



STAT

Fig. 7. Electron micrographs of ruptures of polystyrene films, 12,000X.

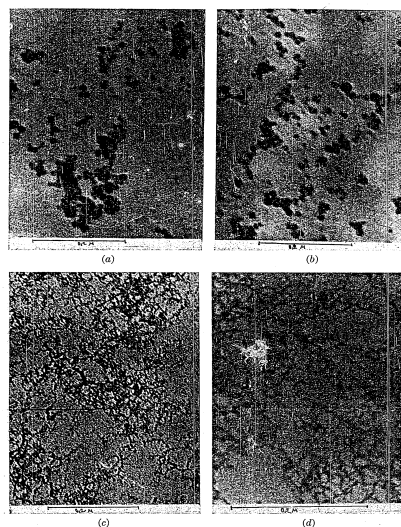


Fig. 8. Electron micrographs. (a) Polyacrylic acid 120,000X. (b) Polyacrylate of barium 120,000X. (c) Polyacrylate of sodium 120,000X. (d) Polyacrylate of cesium 180,000X.

Further studies were directed toward exploring structural features of native cellulose in connection with the interesting studies of K. Meyer and G. Badenhitzen¹ on initiation of native cellulose structure in regenerated cellulose. It is known that such structural changes take place in the swollen fibers at high temperatures. It indicates that the native cellulose modification is thermodynamically stable.

Figure 3 shows the x-ray diffraction patterns of a highly oriented, regenerated cellulose fiber (a); the same fiber after immersion in glycerol for two hours at 250° (b), and a sample of ramie cellulose (c). The x-ray diffraction patterns of these fibers show that it is possible thus to obtain a native cellulose modification of a highly oriented regenerated cellulose and to get rather complete identity of structure as well as of the degree of molecular chain orientation of the fiber. The structural identity is confirmed by the agreement of corresponding interplanar distances (see Table I), and the high degree of orientation, by the distinctness of the pattern. A question arises, in this connection, as to what are the differences and similarities in the structure of these fibers. In this case, the difference lies in the fact that regenerated cellulose fibers are produced in a chemical way and thus, as was mentioned above, we know their phase structure, while the structural history of a native fiber in the concerned region is, unfortunately, not known to us. If we examine the said x-ray patterns from the point of view of formal geometry, we may say they are analogous to the patterns of crystalline substances. One of these patterns definitely corresponds to the amorphous state of cellulose, but we have no reasons to believe that the structure of native cellulose is a crystalline one. We tried to check whether these structural changes are reversible.

Figure 4 shows the x-ray diffraction patterns of a highly oriented regenerated cellulose fiber (a), of the same fiber on its transformation into a native cellulose modification (b), of the same fiber on transformation back to a modification of regenerated cellulose by treatment in 16% for 15 minutes (c), and, finally, after reconversion, by heating in glycerol at 250°C. again, back into a native cellulose modification (d). It may be seen from these data that the cycle of structural transitions from regenerated cellulose into a native cellulose modification and back is a closed one and may be repeated many times. But, in contrast to the direct transition which requires an increase of kT value to overcome the barrier of chain rotation, the reverse transition to the regenerated cellulose occurs spontaneously, as swelling in alkali facilitates the transition.

The results of these investigations confirm V. A. Kargin's conclusion² that native cellulose differs from regenerated cellulose, not by phase structure, but by the configuration of units in the macromolecular chain, each species having its own equilibrium form.

In spite of a good agreement of structural and mechanical data, we considered it necessary to investigate the thermodynamical properties of cellulose to get a final proof of the ideas expressed about the phase structure of cellulose.

It has been shown³ that thermochemical methods of investigation, e.g., the measurement of solution heat, are very useful, having been used successfully in studying the phase structure of polystyrenes and polyanilides. Together with the investigation of the structure, these methods can help to answer the question of phase structure of polymers. Here it must be mentioned that the widely used method of measuring the heats of wetting of cellulose cannot be considered reliable, as these values characterize only a certain part of the enthalpy of the system and depend upon the previous history of the sample, its size and surface, and other factors. Therefore, we decided to use the method of measuring integral heats of solution of cellulose in 34% aqueous solutions of quaternary ammonium bases of the type $(C_4H_9)_4N^+OH^-$. The final concentration of cellulose in the solution was also constant ($\sim 1\%$). The weight of the samples was 0.2-0.25 g. The measurements were carried out in an adiabatic calorimeter permitting the measurement of heat evolved up to 0.2 cal. The accuracy of the measurements in studying the cellulose was within 1-2%. The cellulose dissolved completely during the experiment. The integral heats of solution were measured for (1) Regenerated cellulose fibers of different degrees of orientation produced by spinning in a wide range of stretch of 0 to 120% elongation; and (2) viscose fibers of various spinning conditions characterized by different degrees of orientation and different physical and mechanical properties.

The results are listed in Table II and III.

TABLE II

Integral Heats of Solution of Regenerated Cellulose Fibers as a Function of Stretch				
Degree of orientation, % elongation	0	50	75	100
Heat of solution, cal./g. dry wt.	35.84	34.71	35.18	34.67
				34.28

The above results show that the heats of solution vary within the limits of experimental error and that a slight tendency towards lowering the thermal effect with orientation is not characteristic of changing the enthalpy of a substance in the process of crystallization. The results of x-ray investigations, viz., the absence of phase transitions in the cellulose during the process of imparting orientation to the fiber were thus confirmed with the help of quite independent data.

Analogous measurements were made for different types of regenerated cellulose fibers, and x-ray diffraction patterns were obtained for (1) an isotropic fiber spun in an alkaline bath (Fig. 5a), (2) a high tenacity viscose fiber of a medium orientation spun in an acid bath in the presence of salts (Fig. 5b), and (3) a highly oriented super-tenacity viscose fiber spun in a concentrated acid bath (Fig. 5c).

TABLE III

Integral Heats of Solution for Different Types of Regenerated Cellulose Fibers				
Sample	Size of an individual filament	DP	Tenacity kg./mm. ²	Heat of solution, cal./g. dry weight
1	25	300	7.5	35.97
2	18	350	45.0	37.29
3	9	650	90.0	36.88

X-ray patterns of the fibers are quite different. It might seem that such differences in the textures should be reflected in sharp differences in solution heats. This is not the case, however. This is very important, as the values of thermal effects of solutions are found to be practically independent of spinning conditions and of such peculiarities in physical and mechanical properties as size, type of surface, molecular weight, and fiber structure.

Thus, the results of thermodynamical and structural studies of phase structure of cellulose are found to be in good agreement, which permits the following conclusions: (1) The regenerated cellulose fiber does not change its phase condition and remains amorphous over the whole range of stretching from an isotropic to a highly oriented state. (2) Viscose fibers spun under different conditions have the same phase structure.

References

1. V. A. Kargin and N. V. Michailov, *Zhur. Fiz. Khim.*, **14**, No. 2, 195 (1940).
2. V. A. Kargin and D. I. Lel'punskaia, *Ibid.*, **15**, No. 9, 101 (1941). V. A. Kargin, P. V. Koslov, and T. V. Zueva, *ibid.*, **17**, No. 5-6, 318 (1943).
3. N. V. Michailov, V. A. Kargin, V. J. Eljnek, *Studies of High Molecular Substances*, in *Proceedings of the 6th Conference on High Molecular Substances*, Academy of Sciences, U.S.S.R. 1940, p. 281.
4. G. Katz, *The X-Ray Investigations of Colloids and Fibres*, 1937, p. 199.
5. K. Meyer and G. Badenhuizen, *Nature*, **140**, 281 (1937).
6. V. A. Kargin and G. I. Sionynski, *Vysokhi Khim.*, 1955, N7. H. V. Michailov and E. Z. Fainberg, *Kolloid Zhur.* 1956, No. 1.
7. H. V. Michailov, E. Z. Fainberg, *Doklady Akad. Nauk S.S.S.R.*, **109**, No. 6, 1160 (1956).

Synopsis

Earlier in our work with Kargin we expressed for the first time the assumption concerning the amorphous structure of cellulose. This assumption was proved in the case of partially oriented fibers and films of hydrated cellulose on the basis of structural-mechanical data. A perfect reversibility of the orientation of these fibers was clear from these data as well as a far-reaching analogy between the x-ray diagram of isotropic cellulose and similar diffraction diagrams of amorphous rubber and low molecular weight liquids. At present this conclusion is recognized by many research workers and there are no serious objections to it. It was, however, not clear whether it is possible to apply this statement to "perfectly oriented" hydrated cellulose. There had already been obtained textures with a similar or even higher degree of orientation than with native ramie cellulose. The influence of the orientation on the crystallinity of the fibers of hydrated cellulose in the entire range of extension up to 200% was therefore studied. The x-ray investigation of these fibers according to the criteria of Katz showed that the structure of fibers of hydrated cellulose similar to ramie cellulose as determined from the Debye diagram did not differ significantly from the Debye diagrams of the initially isotropic fibers. From this it necessarily follows that during the orientation of the fibers new elements of symmetry do not arise in their structure. Further x-ray research was directed to studying the differences of the phase structure of hydrated cellulose and its structural modification prepared according to the method of Meyer and Badenhuizen by heating completely oriented fibers of hydrated cellulose in a polar liquid. At the same time it was found that the transition of hydrated cellulose to its modification, native cellulose is thermodynamically reversible and that it can be repeated many times. The direct transition of native cellulose to hydrated cellulose occurs spontaneously and is connected only with a decrease of the force acting between the molecules as a result of swelling. The reverse transition, however, requires an increase of the value of ΔT . This is required only by the differing flexibility of the chains of these modifications of cellulose caused by their differing configuration and not at all by a change of the phase structure of the cellulose.

Since the structural criterion is not adequate for the definitive derivation of the phase structure of cellulose, we determined the integral heat of solution of cellulose fibers of differing structure and molecular weight in an aqueous solution of the quaternary ammonium base ($C_2H_5)_4NCl \cdot H_2O$ in an adiabatic calorimeter with sufficiently high precision. The results obtained show that the heat content of hydrated cellulose does not change over a wide range of orientation of the fibers and that it does not depend on the molecular weight of cellulose nor on the history of the fiber. The absolute values of the corresponding quantities for native cellulose differ only slightly. They change continuously and without breaks on transforming native cellulose to hydrated cellulose by often repeated xanthogenation and regeneration under the action of mineral acids, without damaging the fiber structure. At the same time this rules out phase differences in the structure of both modifications, hydrated cellulose and native cellulose.

STAT

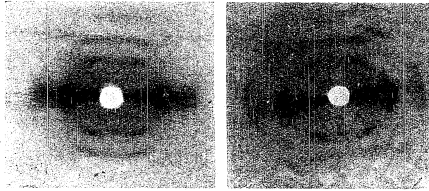


Fig. 1. X-ray diffraction patterns of cellulose fibers: (a) regenerated cellulose fibers stretched to 180% and (b) native ramie cellulose.



Fig. 2. X-Ray diffraction patterns of oriented and isotropic regenerated cellulose fibers: (a) x-ray patterns of an oriented fiber, (b) x-ray pattern of an oriented fiber similar to Debye-diagram, and (c) x-ray pattern of an isotropic fiber.

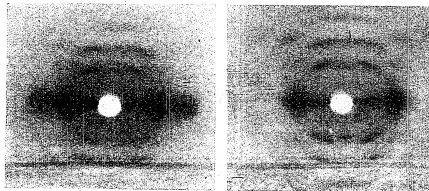


Fig. 3. X-Ray diffraction patterns of various structural modifications of cellulose fibers: (a) x-ray pattern of a highly oriented regenerated cellulose fiber, (b) x-ray pattern of a highly oriented regenerated cellulose fiber whose structure imitates that of native cellulose, and (c) x-ray patterns of native ramie cellulose.

STAT

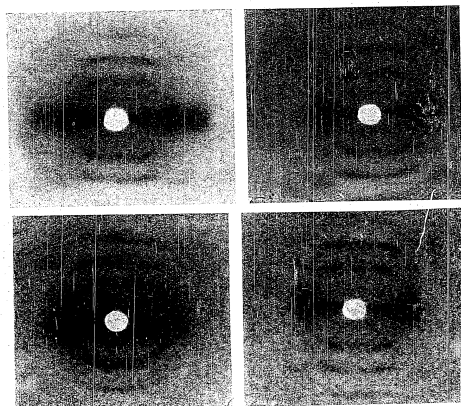


Fig. 4. X-Ray diffraction patterns of regenerated cellulose fibers subjected to structural transformations: (a) x-ray pattern of a highly oriented fiber, (b) x-ray pattern of a highly oriented fiber whose structure imitates that of native cellulose, (c) x-ray pattern of the same fiber treated with 16% NaOH, and (d) x-ray pattern of a highly oriented fiber treated with glycerol at 250°C.

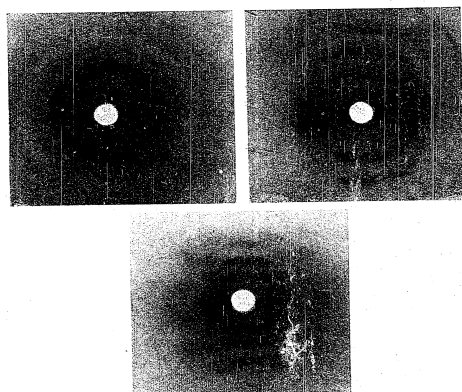


Fig. 5. X-Ray diffraction patterns of different types of rayon: (a) x-ray pattern of an isotropic viscose fiber, (b) x-ray pattern of a high-tenacity viscose fiber, and (c) x-ray pattern of a super-tenacity viscose fiber.

On the Oxidation Mechanism of Rubbers in the Presence of Inhibitors

STAT

L. G. ANGERT and A. S. KUZMINSKII, *Scientific Research Institute of the Rubber Industry, Moscow, U.S.S.R.*

STAT

One of the main causes of irreversible changes in the structure of polymer molecules is the oxidation of the latter by molecular oxygen. The result of this process is the aging of raw and vulcanized rubber, i.e., a loss in important physical properties during storage and use.

Initiation of the oxidation reaction may be due to heat, light, ionizing irradiations, mechanical stresses, and other factors.

As was shown in a number of papers,¹⁻³ free oxidation of rubbers proceeds in the same manner as oxidation of low molecular weight hydrocarbons by the mechanism of degenerated branched chain processes. The kinetics and mechanism of the process change sharply under the influence of various additives, including inhibitors.

Along with the similarities in the oxidation mechanisms of polymers and of low molecular compounds, there are a number of essential differences in the character and kinetics of these processes resulting from the specific nature of polymer molecules.

While the length of the oxidation process chain for free oxidation of tetralin at 100° is equal to 393,⁴ in the case of oxidation of Na-butadiene rubber it is only equal to 8-10.⁵

As a result of this, and also because of the low diffusion coefficient of inhibitors in polymers, the effectiveness of inhibitors in rubber is much less than in low molecular weight hydrocarbons. Consequently, the rational concentration of inhibitors in raw and vulcanized rubbers usually exceeds their concentration in low molecular weight hydrocarbons by 50 to 100-fold.

Due to the great length of the polymer chains, minor chemical transformations resulting from inhibition processes lead to considerable changes in structural and physical properties of the polymers.

Oxidation of raw and vulcanized rubbers during storage and exploitation, resulting in a loss of their plastic-elastic properties, proceeds in the presence of antioxidants and a number of other ingredients acting as inhibitors of chain processes.

In this connection, it is quite obvious how important is the study of the problem of inhibited oxidation and of the mechanism of inhibitory action in creating effective protection of raw and vulcanized rubber against thermal aging.

In recent years, a considerable number of papers⁶⁻¹⁰ have been devoted to investigation of the process of oxidation of rubbers in the presence of inhibitors.

It should be noted that the data given in these papers are often very contradictory, and the schemes describing the mechanism of inhibition are, as a rule, not based on experimental data.

In order to throw light on the mechanism of inhibited oxidation of rubbers, we have attempted in this study to determine the nature and kinetics of the changes undergone by the rubber and inhibitor in the process and also to investigate the dependence of the effectiveness of inhibitors on their concentration and on their molecular structure.

The study of inhibited oxidation is connected with many experimental difficulties, resulting chiefly from the low process rate and the correspondingly small chemical changes of the rubber, the loss of the solubility of the oxidation products and impossibility of their separation, as well as the low concentration of the inhibitors in the rubber.

All these circumstances make it necessary to use many and various methods of research, as well as to modify a number of the accepted methods.

KINETICS OF INHIBITED OXIDATION OF RUBBER

The hydrocarbon of Na-butadiene rubber (further referred to simply as rubber), obtained by thoroughly purifying a commercial polymer, was the object of research. Films 0.15-0.25 mm. thick were studied. The antioxidant most widely used in the rubber industry, phenyl-β-naphthylamine, a secondary aromatic amine, was chosen as the inhibitor for use in the experiments.

The kinetics of the oxidation process were studied by oxygen absorption measured on a volumetric microoxidation apparatus (Fig. 1). The apparatus used was equipped with highly sensitive horizontal manometers, microburets, and barostat vessels, which, combined with the small volume of the system and its isolation from the surrounding atmosphere, provide high sensitivity (up to 0.01 ml. of absorbed oxygen) and great accuracy. The reproducibility of results obtained with the microoxidation apparatus on samples of rubber taken from one and the same refined batch can be seen from the data represented in Figure 2.

Curves 1 and 3 (Fig. 3) describe free oxidation of rubber (in the absence of inhibitors). At 70°C., the rate of oxidation is constant at the beginning of the process; this is a result of the predominant development of primary unbranched reaction chains. This is followed by acceleration of the process and transition to autocatalysis; the latter is characterized by development of a secondary branched chain reaction. The process rate changes by 3 to 4 orders. At a temperature of 150°C., the constant rate period is absent and the process from the very beginning is an autocatalytic one.

The oxidation process at a temperature of 70°C. with a 1% inhibitor content (here, as elsewhere, on the basis of weight) slows down 6.5 times during the period of constant rate. A drop in the oxidation rate takes place as a result of a decrease in the primary chain length due to the increase of the probability of chain termination.

The simultaneously observed increase of the length of the constant rate period (induction period) indicates that the inhibitor also serves to hinder the formation of an intermediate product with chain branching as a result of its decomposition.

A relatively long induction period is observed at 150°C. in the presence of the inhibitor.

Figure 4 shows the kinetics of inhibited rubber oxidation at temperatures of 100-105°C.

The values of oxidation rates are given in Table I.

TABLE I
Rubber Oxidation Rate in the Presence of 1% Phenyl- β -Naphthylamine

T, °C.	$V \times 10^3$, ml. O ₂ /g. sec.
100	0.39
110	0.82
120	1.69
130	4.96
150	13.50

STAT

The mean activation energy of an inhibited oxidation is 21.3 cal./mole. The activation energy of autocatalytic oxidation is only 15 cal./mole.

If the inhibitor is absent at the beginning of the process, but is introduced during the autocatalytic stage of oxidation, then the process is sharply retarded, and, after a short period of time, the rate becomes steady. (Fig. 5). Thus, the inhibiting action of the antioxidant holds also for the autocatalytic process.

The Transformation of Rubber During Inhibited Oxidation

In the process of inhibited oxidation, various oxygen-containing groups accumulate in the polymer molecules. We made a study of the kinetics of accumulation of aldehyde groups (by the bisulfite method), carboxyl groups, and peroxide groups (by the iodine method) which takes place during the oxidation of rubber at a temperature of 120°C. in the presence of 1% phenyl- β -naphthylamine.

From results presented in Figure 6 and Table II, one can see that the greatest amount of oxygen is found in the form of aldehyde groups. The hydroperoxide group content is extremely low (curve 3 is tentatively drawn).

TABLE II
The Rate of Accumulation of Oxygen-Containing Groups During the Oxidation of Rubber in the Presence of 1% Phenyl- β -naphthylamine at 120°C.

Time of oxidation, days	O ₂ found, millimoles/mole				Amount of O ₂ added, millimoles/mole
	Peroxide groups	Aldehyde groups	Carboxyl groups	Total	
1	0.02	1.64	0.58	1.37	3.51
2	0.03	5.50	0.50	3.28	7.08
4	0.04	10.50	0.60	5.89	14.10
8	0.06	15.00	1.20	8.76	28.30

STAT

This was rather unexpected, since, according to the present conception, the role of hydroperoxide in the development of oxidation processes at moderate temperatures is a major one. The observed phenomenon can hardly be explained by the peroxide decomposition of peroxide with formation of aldehydes, as the rate of such a reaction is rather slow under the given test conditions. One could believe that the absence of peroxides is due to their interaction with inhibitor resulting in the formation of stable products, i.e., in the inhibition of the process. However, a detailed investigation of the effect of phenyl- β -naphthylamine on the rate of decomposition of rubber hydroperoxides in solid rubber in an atmosphere of pure nitrogen showed that phenyl- β -naphthylamine does not react with rubber peroxides. From the above data we may conclude that the aldehyde, but not the peroxide, is the main primary product of the inhibited oxidation of polymer.

By the infrared spectroscopy method, we were able to discover in the oxidized rubber the appearance of some amounts of carboxyl groups (see Figure 8; absorption band spectra in the neighborhood of 3400 cm.⁻¹).

It should be pointed out that, during autocatalytic oxidation at temperatures of 100–140°C., the hydroperoxide groups contain only a small amount of oxygen, the bulk of the oxygen being found in carbonyl, carboxyl, and ether groups.^{1,11}

The structural transformations of polymer molecular chains were studied from the produced changes during oxidation in the solubility of the polymer in benzene (the initial polymer was completely soluble), the viscosity of its benzene solutions, and the equilibrium modulus of heat vulcanizates, which represents a value proportional to the number of crosslinks in the polymer.

The heat vulcanizates were obtained by heating films of rubber in a press at a temperature of 220°. The modulus determination was made by the creep method.

The results obtained are given in Figures 8 and 9. As has been shown in a number of papers, the oxidation of rubber is accompanied by two simultaneously proceeding processes, i.e., destruction and crosslinking of molecular chains.

In the case of free oxidation of rubber occurring as a result of competition between these two processes, crosslinking predominates; this is distinctly shown by the data depicted in Figure 9 (curve 1). On the other hand, in the presence of an inhibitor, the initial period of oxidation is characterized by clearly marked polymer destruction (Figs. 9 and 10).

According to data obtained from studies of the oxidation of low molecular weight hydrocarbons at high temperatures,^{12,13} molecular chain rupture is connected with the isomerization of the peroxide radical, followed by its decomposition. Further crosslinking takes place by interaction of the decomposition products with other molecules or radicals of the polymer. Thus, the formation of a three-dimensional structure is related to the growth of the reaction chain.

The presence of an inhibitor in the system undergoing oxidation leads to a termination of the reaction chain in one of the first links, which contributes to lowering the crosslinking rate, i.e., to a change in the ratio between the rates of crosslinking and of destruction, the role of destruction increasing.

The Behavior of the Inhibitor in the Rubber Oxidation Process

As was established in a number of our previous studies,^{4,14} in the course of rubber oxidation the inhibitor is used up and it attaches itself to the molecules of the rubber.

It was also shown that, in the presence of 0.5–0.7% of an inhibitor, the rate of consumption of a free inhibitor is equal to the rate of combination with rubber and has an approximately constant value which is independent of the initial concentration.^{14–17} At the same time, the free phenyl- β -naphthylamine was determined by colorimetric analysis for the colored product of the combination of the inhibitor with a diazo component. The relationship found for the rate of consumption of the free inhibitor when its content in the rubber is low made it possible to calculate the rate of initiation of the oxidation process, as well as to establish the effect on the rate of initiation of such important factors, as the nature of the polymer, mechanical stresses, oxygen concentration, etc.

Enol?

If, however, the behavior of an inhibitor at large initial concentration is exposed, then the pattern changes essentially. Curves, characterizing the kinetics of combination of phenyl- β -naphthylamine with rubber (curve 1) and the kinetics of free amine consumption (curve 2) at initial concentrations of 0.7, 1.0 and 4 weight % at a temperature of 120°C. are presented in Figure 11.

The determination of amine was made by nitrogen content. Free amine was in an extract of oxidized samples of rubber determined by the Duma micromethod; combined amine was determined by the Kjeldahl micromethod.

The fact that the total of the free and the combined nitrogen corresponds to the original content (curve 3) is evidence that the methods used are sufficiently accurate.

By the term combined nitrogen is meant nitrogen entering into the molecule of an amine which is combined with the rubber or one which remains free.

When the inhibitor content exceeds 0.75%, the kinetics of its combination with the polymer are nonlinear. The rate of inhibitor consumption becomes a function of its initial concentration. The last shows that, under these conditions, the inhibitor undergoes additional transformations. It follows, then, that it is necessary to determine whether all the free nitrogen is in the molecules of the unchanged phenyl- β -naphthylamine or whether nitrogen containing amine conversion products also accumulate in the extract.

In order to ascertain this, the data on kinetics of free nitrogen consumption, as determined by the Duma method, were compared with the colorimetrically determined kinetics data which show the quantity of free phenyl- β -naphthylamine (Fig. 12). On the basis of the results of experiments conducted at 130°C., it can be said that there is quite a large divergence between the two kinetic curves. The greater the initial concentration of the inhibitor in the rubber, the larger is the above divergence between the curves. The total quantity of free nitrogen does not correspond to that contained in the molecules of phenyl- β -naphthylamine. It follows, then, that nitrogen is present, not only in the unchanged molecules of the amine, but also in other compounds representing amine-conversion products accumulated during the inhibited polymer oxidation process.

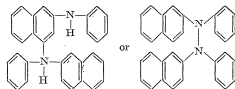
In order to understand the mechanism of the action of the inhibitor, it is extremely important to determine the nature of its conversion products. We succeeded in obtaining some data on this by spectroscopic analysis of a rubber extract which had been oxidized in the presence of an inhibitor. Infrared absorption spectra of phenyl- β -naphthylamine and of an extract of oxidized rubber are given (Fig. 13).

All infrared absorption spectra were obtained with a IKS-2 two-beam spectrograph. The spectra of the inhibitor were obtained on solid samples in the form of thin films on a KBr plate. Films 20-40 μ thick were used for determining rubber spectra.

For comparison, the spectrum of phenyl- β -naphthylamine after oxidation with molecular oxygen is also shown.

On comparing the spectrum of the extract with that of the original amine, one may note a decrease in the N—H bond concentration (3430 and 890 cm^{-1}), a sharp increase in the C—N or N—N (1260 cm^{-1}) bond concentrations, and the appearance of absorption bands which correspond to α - β -substituted naphthalene nuclei oscillations (750-770 cm^{-1}).

It is noteworthy that changes observed in the spectrum of oxidized phenyl- β -naphthylamine are completely similar to those described above. Thus, in both cases one can assume the formation of products of the type:



In the ultraviolet region, the spectra of all the three products studied were identical, an indication of the absence of any changes in the aromatic nuclei.

In studying the effect of phenyl- β -naphthylamine concentration on the kinetics of rubber oxidation, we discovered a marked concentration dependence of the effectiveness of the inhibitor (Fig. 14). The curves describing the dependence of the rate of oxygen absorption by the polymer and also the accumulation of peroxide and aldehyde groups upon the inhibitor concentration have a minimum at a concentration of 1% (Fig. 15). (The rates were obtained from the initial portions of the kinetic curves.) The left, descending branch of the curve is typical of such a relationship for inhibited processes.

As a rule, however, when a certain concentration is reached, a phenomenon of "saturation" is observed in the process of inhibition. A further increase in the content of the inhibitor has practically no effect on the rate of the process. However, in the case of inhibited oxidation of rubber, an increase of the inhibitor content above the concentration of "saturation" leads to some increase in the rate of oxidation. Such a phenomenon may result from the action of molecular oxygen on the inhibitor molecules under the experimental conditions, with formation of active radicals capable of serving as initiators of polymer oxidation. Thus, the inhibitor simultaneously exerts an inhibiting and an initiating effect on the oxidation of rubber. In all cases, the former prevails over the latter.

However, since the initiating effect of the amine increases infinitely with increasing amine concentration, the inhibiting effect of the amine at a concentration close to saturation starts to decrease.

EFFECT OF A NUMBER OF PHENYL- β -NAPHTHYLAMINE DERIVATIVES ON THE OXIDATION OF RUBBER

On the basis of the fundamental concepts of organic chemistry, the inhibiting action of amines is usually related to abstraction of the amine hydrogen atom from their molecules. We thought it interesting to estimate experimentally the role of mobile hydrogen atoms in the phenyl- β -naphthylamine molecule during the process of inhibition of rubber oxidation. With this in view, we studied the inhibiting action of the following two phenyl- β -naphthylamine derivatives, in each of which one of the most mobile hydrogen atoms is absent: phenyl- α -methyl- β -naphthylamine and *N*-methyl-phenyl- β -naphthylamine.

In Figure 16 are presented results obtained during the determination of the length of the induction period for the oxidation of natural rubber hydrocarbon containing the compounds mentioned and also phenyl- β -naphthylamine in the amount of 10.0 millimoles/l. It is evident that the absence of amine hydrogen leads to practically full suppression of the amine inhibition power, i.e., primarily the N—H bond is responsible for chain termination. Some decrease in the inhibitor effectiveness is also observed in the case of substitution of the hydrogen atom in the α -position of the naphthalene nucleus. This may be connected partially with the participation of the atom in the process of inhibition and also with its influence on the mobility of the amine hydrogen.

STAT

STAT

STAT

L. G. ANGERT & A. S. JUZMINSKII

It is known that secondary amines do not inhibit polymerization and also do not influence the process of thermal crosslinking of polymers if oxygen is absent from the system.^{10,11} On the basis of these facts it can be stated with a high degree of certainty that abstraction of hydrogen from the amine occurs as a result of the interaction of the latter with the oxygen-containing radical of the polymer chain.

On abstraction of the hydrogen atom from the amino group a phenyl-naphthyl-nitrogen radical is formed which, as was shown above, combines with the polymer chain.

In order to determine the role of this radical in the process of inhibition, we investigated the inhibiting action of its analogue, the diphenyl-nitrogen radical, which is formed under conditions of oxidation as a result of decomposition of tetraphenylhydrazine. As was proved experimentally the diphenyl-nitrogen radicals inhibit the oxidation of rubber, and their effectiveness even exceeds, to some extent, the effectiveness of diphenylamine. This serves to prove that the radical of the inhibitor also terminates the reaction chains, recombining with the radicals of the hydrocarbon undergoing oxidation.

Data exist, which show that, in the absence of oxygen, tetraphenylhydrazine, as well as the amines, has no effect on polymerization. This gives reason to assume that the diaryl-nitrogen radical may, as does the amine, interact only with hydrocarbon radicals containing oxygen.

The Effectiveness of Inhibitors as a Function of Their Molecular Structures.

In as much as the inhibition of an oxidation process by secondary amines is connected with rupture of the N—H bond and formation of a radical with a free valence at the nitrogen atom, the effectiveness of such inhibitors must increase with decreasing activity of the radical formed and correspondingly decreasing N—H bond energy. From contemporary ideas on the relationship between the reactivity of molecules and their structure, it follows that the relative activity of the radical A· and the energy of the A—H bond, which is a function of the activity, decrease with an increase in the conjugation energy of the radical "free" electron.

To throw light on the relationship between the effectiveness of inhibitors of the secondary amine type and the above mentioned factors, we investigated the inhibiting action of a series of amines, having different numbers of aromatic nuclei per molecule. This series consisted of the following compounds: diphenylamine, phenyl-β-naphthylamine and di-β-naphthylamine. The evaluation of the relative reactivity of these amines in reactions connected with N—H bond rupture was by the speed of their interaction with α,α-diphenyl-β-picrylhydrazyl, a low-activity radical.

According to literature data,¹² this radical reacts readily with amines and, on abstracting the hydrogen atom from the amino group, is transformed into the saturated molecule, α,α-diphenyl-β-picrylhydrazine. The kinetics of such a reaction can be followed easily by measuring the gradual decrease in the intensity of the violet color of the benzene solutions of both components, which is connected with the disappearance of hydrazyl.

Figure 17 shows the kinetics of the reaction of the hydrazyl with phenyl-β-naphthylamine and *N*-methylphenyl-β-naphthylamine. (Photometric measurements of the solutions were made with a spectrophotometer or a photocolorimeter). As is evident from the data, the hydrazyl does not react with *N*-methylphenyl-β-naphthylamine.

On the other hand, of lead dioxide (an oxidizing agent used for preparation of hydrazyl from hydrazine) is added to the solution in which the reaction between phenyl-β-naphthylamine and hydrazyl has been carried out, the violet colour of the solution is restored.

The two above-mentioned results confirm the data attesting to the fact that the reaction of the hydrazyl with amines proceeds with loss of the amine hydrogen and conversion of the hydrazyl into a saturated molecule of hydrazine. The hydrazyl itself does not undergo any change in the benzene solution over a long period of time (Fig. 17, curve 1). The curve describing the kinetics of the reaction of the hydrazyl with phenyl-β-naphthylamine in vacuo (10⁻² mm. Hg) coincides with the kinetic curve, given in Figure 17 (curve 3); it follows from this that the nature of the process does not depend upon the presence of oxygen.

The results of the study of the kinetics of interaction of the hydrazyl with amines differing in the conjugation effect in the radical, are given in Figure 18. The molar ratio of the hydrazyl and amine is 1:1. The initial portions of the kinetic curves are satisfactorily described by the equation for reactions of the second order. The calculated constants of the reaction rate are for diphenylamine, phenyl-β-naphthylamine, and di-β-naphthylamine—0.31, ±1.39, and ±3.42/mole sec., respectively.

On the basis of these data the relative reactivities of the compounds investigated, as given by the rate of the reactions connected with loss of amine hydrogen, may be estimated to be approximately 1:4.5:11.

Investigation of the inhibiting effect of amines on rubber oxidation yielded the results shown in Figure 19. (The concentration of the inhibitors was 40 millimoles/l.). Examination of the curves leads to the conclusion that an increase in the effect of conjugation in the radical does contribute to the growth of the inhibiting power of amine. The ratio of the rubber oxidation rates in the presence of three amines is 1:0.19:0.10. If their inhibiting action is estimated to accord to the reciprocal of the oxidation rate, it will be represented by the relative values, 1:5.2:9.7. The latter ratio is obviously very close to that of the rates that describe the reactivity of amines. This attests to the fact that there is a direct relationship between the reactivity and the inhibiting power of the compounds investigated.

The N—H bond energy must also change if various substituents are introduced in the *p*-position to the benzene nucleus. The effect of this structural factor on the mobility of the amine hydrogen and on the inhibiting power of the amine was investigated in the following compounds: phenyl-β-naphthylamines, *p*-tolyl-β-naphthylamine, *p*-chlorophenyl-β-naphthylamine, *p*-methoxy-β-naphthylamine, *p*-oxyphenyl-β-naphthylamine, and *o,o,p*-trinitrophenyl-β-naphthylamine.

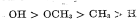
Evaluation of the mobility of the hydrogen atoms of the amino group on the basis of the reaction with hydrazyl was made for only a part of the amines. The molar ratio of hydrazyl and amine was 1:10. The results of the study of the kinetics of this reaction (Fig. 20) show that the initial portion of the curve may be described by a first-order reaction equation. The rate constants for phenyl-β-naphthylamine, *p*-tolyl-β-naphthylamine, and *p*-methoxyphenyl-β-naphthylamine— 0.4×10^{-3} , 1.03×10^{-3} , and 7.73×10^{-3} /sec., respectively.

The reaction with *p*-oxyphenyl-β-naphthylamine under these conditions took place instantaneously.

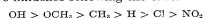
STAT

STAT

Thus, the substituents can be arranged in the following order, according to their influence on the increase in the reactivity of the molecule in reactions connected with rupture of the N—H bond:



The kinetics of rubber oxidation in the presence of the amines listed above are described in Figure 21. The content of the inhibitor was 10 millimoles/l. The oxidation rate, as well as the length of the induction period differs greatly in the presence of various amines. The main conclusion one can draw from the results obtained is that the inhibiting action of the amines depends on the nature of the *p*-substituents in the benzene nucleus, the positive influence having the order:



The position of the substituents in this series coincides with their positions if arranged according to their effect on the reactivity of amines and also according to the electron donor properties of the radicals with respect to the benzene nucleus. It follows, then, that an increase in the electron density at the carbon atom joined to the nitrogen atom leads to the weakening of the N—H bond and, thus, to an increase in the inhibiting power of the amine.

The rubber oxidation inhibiting properties of a number of amines was also studied with respect to the structural changes occurring in the rubber.

Curves depicting the kinetics of change in the number of crosslinks present in a unit volume of a heat vulcanizate undergoing oxidation in the presence of various inhibitors are shown in Figure 22. The data obtained show that the inhibitors, if arranged according to their influence on the change in rubber structure, increase in the same order as was established in studying the kinetics of polymer oxidation.

Among the phenyl- β -naphthylamine derivatives investigated, the most effective as an inhibitor is *p*-oxyphenyl- β -naphthylamine, which should find wide commercial application in the near future.

ON THE MECHANISM OF INHIBITED OXIDATION

The following scheme of the oxidation of rubber in the presence of inhibitors of secondary amine type may be proposed on the basis of the experimental data presented above and also on applying the theory of the mechanism of oxidation of low molecular weight hydrocarbons developed by N. N. Semenov:²¹

- (1) $\text{RH} + \text{O}_2 \longrightarrow \text{R}^\cdot + \text{HO}_2^\cdot$
- (2) $\text{R}^\cdot + \text{O}_2 \longrightarrow \text{ROO}^\cdot$
- (3) $\text{ROO}^\cdot + \text{HN}(\text{A})_2 \longrightarrow \text{ROOH} + (\text{A})_2\text{N}^\cdot$
- (4) $\text{ROO}^\cdot \longrightarrow \text{R}_2\text{CHO} + \text{R}_2\text{O}^\cdot$
- (5) $\text{R}_2\text{O}^\cdot + \text{HN}(\text{A})_2 \longrightarrow \text{R}_2\text{OH} + (\text{A})_2\text{N}^\cdot$
- (6) $\text{R}_2\text{OH} \xrightarrow{\text{O}_2} \text{aldehyde}$
- (7) $\text{R}_2\text{CHO} \xrightarrow{\text{O}_2} \text{acid}$
- (8) $\text{HN}(\text{A})_2 + \text{O}_2 \longrightarrow \text{HO}_2^\cdot + (\text{A})_2\text{N}^\cdot$
- (9) $(\text{A})_2\text{N}^\cdot + \text{O}_2 \longrightarrow (\text{A})_2\text{N}(\text{O}_2)^\cdot$
- (10) $(\text{A})_2\text{N}(\text{O}_2)^\cdot + \text{RH} \longrightarrow \text{R}^\cdot + (\text{A})_2\text{N}(\text{O}_2)\text{H}$
- (11) $2(\text{A})_2\text{N}^\cdot \rightleftharpoons (\text{A})_2\text{N}-\text{N}(\text{A})_2$
- (12) $(\text{A})_2\text{N}^\cdot + \text{ROO}^\cdot \longrightarrow \text{ROON}(\text{A})_2$
- (13) $(\text{A})_2\text{N}^\cdot + \text{R}_2\text{O}^\cdot \longrightarrow \text{R}_2\text{ON}(\text{A})_2$
- (14) $(\text{A})_2\text{N}(\text{O}_2)^\cdot + \text{R}^\cdot \longrightarrow (\text{A})_2\text{N}(\text{O}_2)\text{R}$

where R is a hydrocarbon radical, $\text{HN}(\text{A})_2$ is an inhibitor molecule, $(\text{A})_2\text{N}^\cdot$ is an inhibitor radical, and $(\text{A})_2\text{N}(\text{O}_2)^\cdot$ is an oxygen-containing inhibitor radical.

In a number of papers by N. N. Semenov *et al.* it is shown that chain initiation in oxidation processes may occur as a result of the interaction of saturated molecules accompanied by formation of the low activity radical HO_2^\cdot and a primary hydrocarbon radical.

The peroxide radical, formed by attachment of oxygen to the polymer radical, may undergo two types of conversions [reactions (3) and (4)]. The presence of a large number of aldehyde groups, a low hydroperoxide content, and, also, the destruction of molecular chains are evidence that the peroxide radical reacts primarily according to reaction (4) and not according to reaction (3). Although, for low molecular weight hydrocarbons, reaction (4) takes place at high temperatures, it should proceed for polymers even at moderate temperatures, since monomolecular decomposition in a polymer medium is made easier by a greater period of life of the radicals.

As was found on investigation of propylene oxidation,¹³ degenerated chain branching may occur as a result of decomposition of aldehydes accumulated in the system.

It may be assumed that such a phenomenon also takes place in rubbers after the inhibitor is exhausted.

The inhibition of the process takes place as a result of reaction (5) or (3) and the succeeding chain termination reactions (11–14). The rate of reaction (5) depends on the N—H bond energy, which, as was shown above, is determined by the structure of the radical $(\text{A})_2\text{N}^\cdot$. Reaction (5) will naturally proceed the faster, the less is the energy value of that bond. However, this reaction competes with the reaction (8), leading to accumulation of $(\text{A})_2\text{N}^\cdot$ and $(\text{A})_2\text{N}(\text{O}_2)^\cdot$ radicals (the nature of the latter radical is unknown), and to an increase in the rate of chain transfer reaction, (10), *i.e.*, to a decrease in the inhibiting action of the additive. Obviously, the dependence of the inhibitory action of amines on the N—H bond energy will be described by the same curve that was obtained for the concentration dependence of the effectiveness of an inhibitor.

The chain termination reactions also compete among themselves. The relative reaction rate for the recombination of $(\text{A})_2\text{N}^\cdot$ radicals will, to a great extent, increase with an increase in the inhibitor concentration and a decrease in the N—H bond energy. If we assume that product $(\text{A})_2\text{N}-\text{N}(\text{A})_2$ is capable of breaking up into radicals in the same manner as tetraphenylhydrazine, then reaction (11) should be considered to be reversible.

The products of the recombination of inhibitor radicals, together with the oxidation products of the inhibitor itself, are very compounds which were discovered to be present in the extract of oxidized rubber, along with the unchanged molecules of phenyl- β -naphthylamine.

The rest of the termination reactions are related to the attachment of a part of the inhibitor molecule (in particular, nitrogen) to the oxidized polymer molecular chains.

In conclusion, it is necessary to note that the scheme described does not nearly exhaust all possible reactions proceeding during oxidation. We believe only that it depicts the principal course of the process.

STAT

STAT

Synopsis

Free oxidation of rubbers represents a chain process which, at moderate temperatures, consists of two stages. The first stage, constant oxidation rate, is characterized predominantly by the development of an unbranched chain reaction leading to the accumulation of an intermediate compound of low stability. The second stage, autocatalytic oxidation, represents a degenerated branched process, resulting from the decomposition of intermediate products. Inhibitors of the secondary aromatic amine type lower the oxidation rate in the first stage and sharply increase its duration. The inhibited process activation energy is 21.3 kJ/mole. In the inhibited oxidation, the major part of the combined oxygen is contained in the aldehyde groups. In contrast to free oxidation, in which crosslinking of the chains is the dominant process, in inhibited oxidation, the process of destruction of polymer molecules is predominant at first. The inhibited rubber oxidation rate depends on the concentration of the inhibitor. This dependence is described by a curve with a minimum. During the process of the oxidation of rubber, some of the inhibitor combines with the molecules of the polymer, and the rest is subjected directly to the action of molecular oxygen. There is an increase in the rate of rubber oxidation, at inhibitor concentrations above a given level, which is attributable to the initiating action of intermediate radical products of inhibitor oxidation. The inhibitors of the secondary amine type do not interact with stable rubber peroxides and, with hydrocarbon radicals. It was shown, that the N—H bond in the amine molecule is above all responsible for the inhibition effect. It was found that the inhibiting power of amines is a direct function of the mobility of the amine hydrogen. The increase in mobility of this atom is attained by: (1) an increase of the conjugation effect in the inhibitor radical, which results from an increase in the number of aromatic nuclei in the amine molecule; and (2) introduction of electron donor substituents in the position *para* to the secondary amine in the benzene nucleus. The experimental data obtained and also the contemporary theory of the mechanism of oxidation of low molecular weight hydrocarbons made it possible to suggest a chemical scheme of the rubber oxidation mechanism in the presence of inhibitors of the secondary aromatic amine type.

References

1. A. S. Kuzminskii, *Zhur. Obshch. Khim.*, **18**, No. 6, 1054 (1948).
2. A. S. Kuzminskii, T. G. Degteva, and K. A. Lapteva, *Zhur. Priklad. Khim.*, **22**, No. 4, 423 (1949).
3. A. S. Kuzminskii, *Trudy Moskov. Inst. Tonkoj Khim. Tekhnol. im. M. V. Lomonosova*, **1948**, No. 1, 1948.
4. D. G. Krasov, et al., *Doklady Akad. Nauk S.S.S.R.*, **26**, No. 4, 416 (1957).
5. A. S. Kuzminskii, dissertation, Moskov. Inst. Tonkoj Khim. Tekhnol. im. M. V. Lomonosova, Moscow, 1950.
6. J. R. Shelton and W. L. Cox, *Ind. Eng. Chem.*, **46**, 816 (1954).
7. S. Baxter, W. Morgan, and D. S. Roelback, *Rubber Chem. Technol.*, **24**, No. 4, 805 (1951).
8. C. E. Kendall, *Proc. Intern. Congr. Pure and Appl. Chem. 11th Congr. London, 1947* (1953), **5**, 343.
9. Cole and Field, *Ind. Eng. Chem.*, **39**, 174 (1947).
10. L. Bateman, *Trans. Inst. Rubber Ind.*, **26**, No. 3, 246 (1950).
11. M. A. Salimoff, A. P. Postovskaya, A. S. Kuzminskii, and V. M. Tatevskii, *Vestnik MGU*, No. 1, 167 (1957).
12. A. B. Nalbandian and N. V. Tok, *Doklady Akad. Nauk S.S.S.R.*, **85**, 1053 (1952).
13. V. Ya. Stern, *Voprosy Khim. Kinetiki, Ketoliz, i Reaktivnosti Spasobnosti, Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, **1955**, 197.
14. A. S. Kuzminskii and N. N. Lezhnev, *Doklady Akad. Nauk S.S.S.R.*, **69**, No. 4, 557 (1949).
15. A. S. Kuzminskii and N. N. Lezhnev, *Doklady Akad. Nauk S.S.S.R.*, **70**, No. 6, 1021 (1950).
16. A. S. Kuzminskii and N. N. Lezhnev, *Zhur. Fiz. Khim.*, **24**, No. 5, 539 (1950).
17. A. S. Kuzminskii, M. G. Maizels, and N. N. Lezhnev, *Doklady Akad. Nauk S.S.S.R.*, **91**, No. 2, 319 (1950).
18. B. A. Dolgoplosk, *Voprosy Khim. Kinetiki, Ketoliz, i Reaktivnosti Spasobnosti, Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, **1955**, 303.
19. I. A. Shokhin, Dissertation, Moskov. Inst. Tonkoj Khim. Tekhnol. im. M. V. Lomonosova, Moscow, 1950.
20. *Ber. deut. chem. Ges.*, **55**, 628 (1922).
21. N. N. Semenov, *Osnovnykh problemakh Khimicheskoi Kinetiki i reaktivnosti spasobnosti (On Some Problems of Chemical Kinetics and Reactivity)*, Moscow: Izdatel'stvo Akad. Nauk S.S.S.R., 1954.

Discussion

J. Benisek (*Bratislava*): Why does the oxygen not react with all the radicals, even with the formation of hydroperoxides?

A. S. Kuzminskii (*Moscow*): If, in the inhibited oxidation, the peroxide radicals react with the molecules of the inhibitor, an accumulation of the hydroperoxide must occur since the stabilization of the hydroperoxide takes place at the expense of the inhibitor. However, we did not obtain peroxides in the inhibited oxidation. The temperature during the reaction was so low that the peroxides could not possibly decompose. The absence of the stable peroxides indicates that the stabilization of the peroxide radicals is not a fundamental trend of the reaction with the inhibitor. The main trend of this reaction is evidently stabilization of the oxygen radical since we found a large amount of oxygen in the form of aldehydes.

M. Magat (*Paris*): Est-ce qu'il est possible que la réaction $ROO\cdot + HInh \rightarrow ROOH + Inh$ se produise pas avec les inhibiteurs utilisés simplement parce qu'elle serait endothermique?

A. Tkáč (*Bratislava*): In the given reaction scheme the decomposition of the hydroperoxides is not considered. In a reaction mechanism based on the study of the rate of accumulation of the intermediates (aldehydes and hydroxyis), we assume the disintegration of the hydroperoxides if the process follows kinetic equations valid for degenerate branched chain reactions.

Does this difference not depend on the different methods by which the oxidation is followed (following of the total amount of the oxygen consumed) assuming that the primary oxidation products—mainly aldehydes—which determine the nature of the chain mechanism are oxidized in a subsequent reaction to carboxylics?

A. S. Kuzminskii: It is not possible to compare our results about the inhibition of rubber oxidation directly with those of Tkáč and Kelic relating to autocatalytic oxidation. As I stated in my paper, these processes differ not only by their rate but also by their mechanism. The free autocatalytic oxidation of rubber proceeds according to the branched chain mechanism. The inhibited process does not seem to be branched. Its rate remains constant until the inhibitor is entirely exhausted. It is interesting that even in more complicated systems such as multi-component resins the rate of the inhibited oxidation is also constant.

In the oxidation of rubbers two tendencies in the inhibitor action are observed: interruption and oxidation of the reaction chains. Competition of these two tendencies influences the position of the minimum rate of oxidation at some optimum concentration of the inhibitor. It is obvious that this oxidation rate can be approximately determined as a rate of initiation. The ratio of the oxidation rate at another arbitrary concentration of the inhibitor to the minimum rate represents the length of the reaction chain.

Practical doses of the inhibitors in rubber correspond to their optimum concentrations in the sense I have stated. The first stable products of the inhibited oxidation of rubber are aldehydes which accumulate in considerable amounts. Hydroperoxides are formed but in negligible amounts. Their decomposition is not great as was proved by a special series of experiments.

STAT

STAT

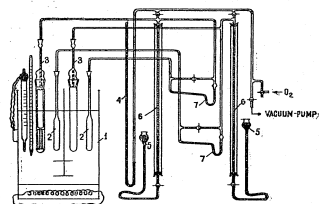


Fig. 1. Microoxidation apparatus: (1) thermostatically controlled vessel; (2) barostat vessel; (3) reaction vessel; (4) "U"-tube manometer; (5) bulb for mercury; (6) microburet; (7) manometer.

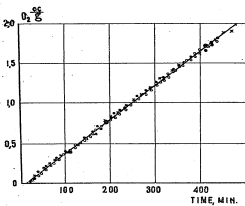


Fig. 2. Kinetics of oxidation of various samples of rubber at 130°C.

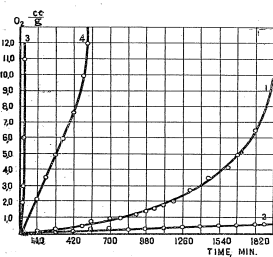


Fig. 3. Kinetics of oxidation of rubber: (1) pure rubber (70°C); (2) rubber with 1% phenyl- β -naphthylamine (70°C); (3) pure rubber (150°C); (4) rubber with 0.5% phenyl- β -naphthylamine (150°C).

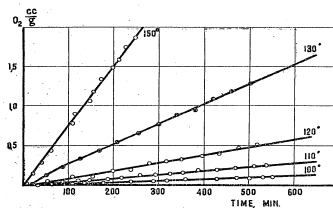


Fig. 4. Kinetics of oxidation of rubber containing 1% phenyl- β -naphthylamine.

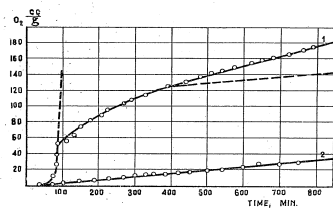


Fig. 5. Kinetics of oxidation of rubber at 130°C: (1) phenyl- β -naphthylamine introduced in the autocatalytic stage; (2) phenyl- β -naphthylamine present from the very beginning of the oxidation process.

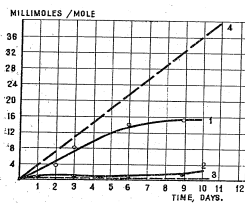
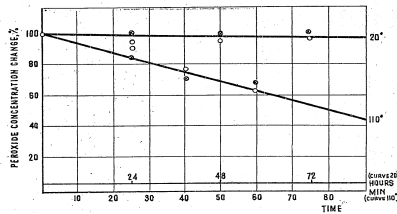


Fig. 6. Kinetics of accumulations of oxygen-containing groups in oxidation of rubber containing 1.0% of phenyl- β -naphthylamine at 120°C: (1) aldehyde groups; (2) carboxyl groups; (3) peroxide groups; (4) oxygen absorption.



STAT

Fig. 7. Reaction of rubber peroxides with phenyl-β-naphthylamine: (●) peroxide concentration in the absence of phenyl-β-naphthylamine; (○) peroxide concentration in the presence of phenyl-β-naphthylamine.

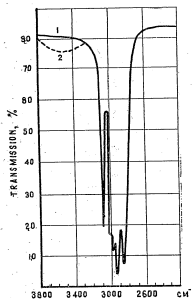


Fig. 8. Infrared spectrum of rubber absorption: (1) before oxidation; (2) after oxidation (9 days, 120°C.).

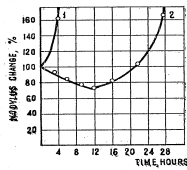


Fig. 9. Kinetics of structural change in the oxidation of heat vulcanizate (130°C.): (1) in the absence of inhibitor; (2) in the presence of 1.0% phenyl-β-naphthylamine.

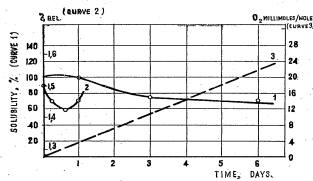


Fig. 10. Kinetics of the change in the structure of rubber in oxidation (120°C.).

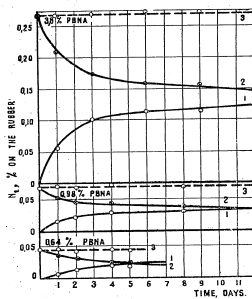


Fig. 11. Kinetics of change of nitrogen concentration during oxidation of rubber in the presence of various amounts of an inhibitor (120°C.): (1) combined nitrogen; (2) free nitrogen; (3) total nitrogen.

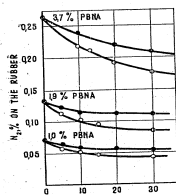


Fig. 12. Kinetics of free nitrogen consumption in oxidation of rubber in the presence of various amounts of phenyl-β-naphthylamine (130°C.): (○) colorimetric data; (●) data obtained by Duma's method.

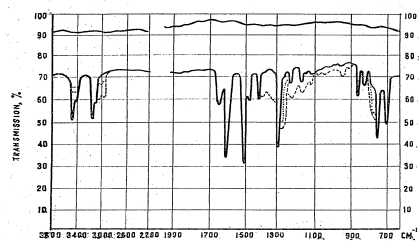


Fig. 13. Infrared absorption spectra: (—) phenyl-β-naphthylamine; (---) extract of rubber oxidized 9 days at 120°C; (—) phenyl-β-naphthylamine after oxidation 70 hours at 140°C.

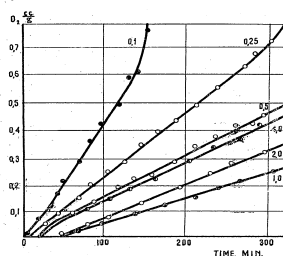


Fig. 14. Oxidation of rubber containing various amounts of phenyl-β-naphthylamine at 120°C.

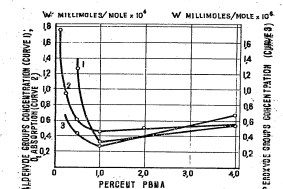


Fig. 15. Dependence of the rate of oxidation of rubber on the concentration of the inhibitor at 120°C.

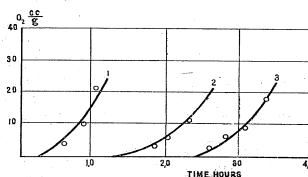


Fig. 16. Duration of the induction period in oxidation of natural rubber with an inhibitor content of 10 millimoles/l. (120°C); in the presence of (1) N-methyl phenyl-β-naphthylamine, (2) phenyl-α-methyl-β-naphthylamine, and (3) phenyl-β-naphthylamine.

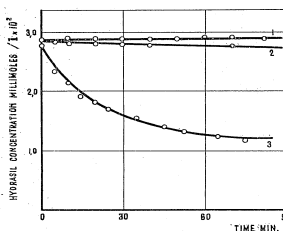


Fig. 17. Kinetics of the reaction of hydrazyl with amines (20°C): (1) pure hydrazyl; (2) hydrazyl with N-methyl-phenyl-β-naphthylamine; (3) hydrazyl with phenyl-β-naphthylamine.

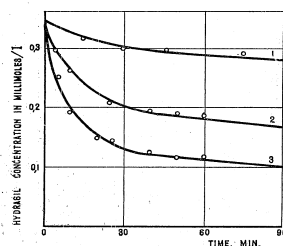


Fig. 18. Kinetics of reaction of hydrazyl with amines (40°C): (1) diphenylamine, (2) phenyl-β-naphthylamine, and (3) di-β-naphthylamine.

STAT

STAT

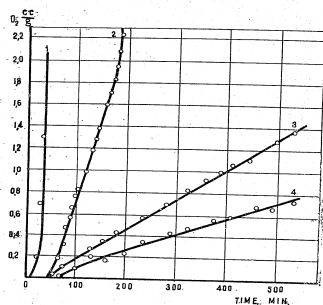


Fig. 19. Kinetics of oxidation of rubber containing various inhibitors 120°C.: (1) no inhibitor, (2) diphenylamine, (3) phenyl-β-naphthylamine, and (4) di-β-naphthylamine.

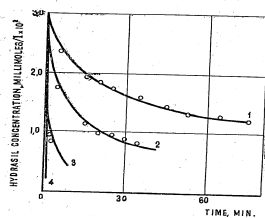


Fig. 20. Kinetics of reaction of hydroxyl with amines 20°C.: (1) phenyl-β-naphthylamine, (2) p-tolyl-β-naphthylamine, (3) p-methoxyphenyl-β-naphthylamine, and (4) p-oxyphenyl-β-naphthylamine.

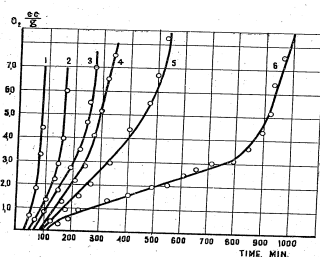


Fig. 21. Kinetics of oxidation of rubber in the presence of phenyl-β-naphthylamine derivatives 120°C.: (1) phenyl-β-naphthylamine, (2) p-chlorophenyl-β-naphthylamine, (3) phenyl-β-naphthylamine, (4) p-tolyl-β-naphthylamine, (5) p-methoxyphenyl-β-naphthylamine, and (6) p-oxyphenyl-β-naphthylamine.

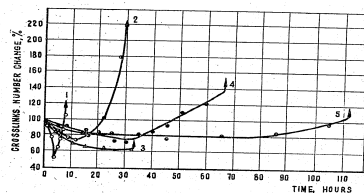


Fig. 22. Structural changes in heat vulcanizates during oxidation in the presence of inhibitors 120°C.: (1) diphenylamine, (2) phenyl-β-naphthylamine, (3) p-tolyl-β-naphthylamine, (4) p-methoxyphenyl-β-naphthylamine, and (5) p-oxyphenyl-β-naphthylamine.

fixed by their polar group. Figure 7 shows the change in the relative viscosity of the solutions of polymethylacrylate in toluol in the process of adsorption by aluminum oxide. In this case the substance adsorbed may be completely washed out fraction by fraction with a good solvent as, for instance, chloroform, which is particularly important for fractionating the substances by means of adsorption.

Conclusions

The process of adsorption of some high molecular substances by carbon black and hydrophobic aluminum oxide from dilute solutions was investigated. It has been proved that there exists a direct proportional relationship between the square of the characteristic viscosity and the time required for complete adsorption of the substance from the solution. The influence of the solvents as well as the size of the alcohol radical of polyethers of the acrylic and methacrylic acids on the adsorption process were also studied. It is proved that the hydrophobic aluminum oxide may be employed as an adsorbent of high polymers from solutions.

References

1. M. C. Brooks and R. M. Badger, *J. Am. Chem. Soc.*, **72**, 4384 (1950).
2. D. W. Bannister, C. S. G. Phillips, and R. J. P. Williams, *Anal. Chem.*, **26**, 1451 (1954).
3. M. A. Golub, *J. Polymer Sci.*, **11**, 583 (1953).
4. I. M. Kolthoff, R. G. Guttmacher, and H. Kahn, *J. Phys. Coll. Chem.*, **55**, 1240 (1951).
5. I. M. Kolthoff and R. G. Guttmacher, *J. Phys. Chem.*, **56**, 740 (1952).
6. G. Kraus and J. Dugone, *Ind. Eng. Chem.*, **47**, 1809 (1955).
7. H. H. G. Jellinek and H. L. Northey, *J. Polymer Sci.*, **14**, 583 (1954).

Synopsis

Adsorption experiments were made to determine the time required for a complete adsorption of certain highly molecular substances from solutions. Aluminum oxide was preliminarily subjected to hydrophobization by caproic acid. Samples of polystyrene, polyisoprene, and polyethers of acrylic and methacrylic acids, ranging from methyl to heptyl inclusive, were taken as objects of the experiments. In all cases the time required for a complete extraction of the substances from solution was shown to be directly proportional to square of the characteristic viscosity. "Bad" solvents take a shorter time to effect a complete adsorption. The investigation of adsorption of polyethers of acrylic and methacrylic acids has shown that the increase in the alcohol radical influences the velocity of the adsorption process as a whole in different ways. While the increase in the alcohol radical of the polyacrylic ethers reduces the time required for a practically complete adsorption of the substance, in the case of polyethers of methacrylic acid the reverse relation was observed. Hydrophobic aluminum oxide is shown to adsorb polymethyl acrylate from solution reversibly.

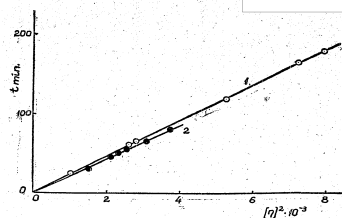


Fig. 1. Relation of the time of full adsorption of polystyrene to the characteristic viscosity squared. The solvent is benzol. (1) Polystyrene fractions, (2) Polystyrene. The initial solution concentration $C = 0.1\%$.

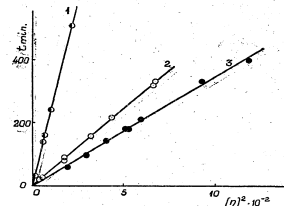


Fig. 2. Relation of the time of full adsorption to the characteristic viscosity squared. (1) Polyisoprene, $C = 0.1\%$. (2) Polystyrene fractions, $C = 0.25\%$. (3) Polystyrene, $C = 0.25\%$. The solvent is benzol.

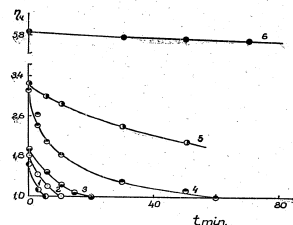


Fig. 3. The change in the relative viscosity of polymethylacrylate solution in the adsorption process in various solvents. (1) Toluol. (2) Butyl acetate. (3) Methyl ethyl ketone. (4) Acetone. (5) Benzol. (6) Chloroform. $C = 0.25\%$.

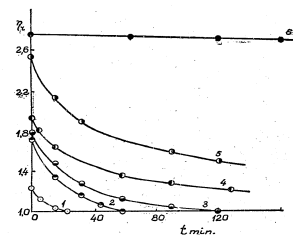


Fig. 4. The change in the relative viscosity of polymethyl methacrylate solutions in the process of adsorption in various solvents. (1) Butyl acetate. (2) Acetone. (3) Methyl ethyl ketone. (4) Toluol. (5) Benzol. (6) Chloroform. $C = 0.25\%$.

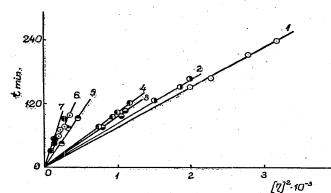


Fig. 5. The relation of the time of full adsorption to the square of the characteristic viscosity for polyethers of acrylic acid. (1) Methyl. (2) Ethyl. (3) Propyl. (4) Butyl. (5) Amyl. (6) Hexyl. (7) Heptyl.

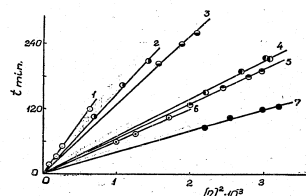


Fig. 6. The relation of the time of full adsorption to square of the characteristic viscosity for polyethers of methacrylic acid. (1) Methyl. (2) Ethyl. (3) Propyl. (4) Butyl. (5) Amyl. (6) Hexyl. (7) Heptyl.

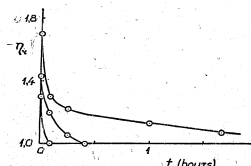


Fig. 7. The change in the relative viscosity of the solutions of polymethylacrylate of different molecular weight in the process of adsorption by aluminum oxide.

Cold-Drawing of Glass-Like and Crystalline Polymers

J. S. LAZURKIN,* *Institute of Atomic Energy, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.*

The phenomenon of cold-drawing of polymers, widely used in the technology of synthetic fibres, is of broad interest, which surpasses the field of *The major part of these investigations, which form the basis for the present paper, were done in cooperation with G. P. Ushakov.

the above-mentioned application. Its study is of the same importance for polymers as is the study of plastic behavior for metals. The theory of cold-drawing is an important branch of the theory of mechanic properties of polymer substances, which must be understood in order to elucidate the problems of brittle and non-brittle behavior of solid polymer materials, the influence of orientation on the mechanical properties of polymer glasses, etc.

For a long time, only the cold-drawing of crystalline polymers¹⁻⁴ was studied. Then some papers were published on cold-drawing of glass-like polymers, where the phenomenon has been called "forced elasticity"⁵⁻⁹ (see also review¹⁰). In recent years, attempts have been made to put forth a theory which could explain the phenomenon in both groups of compounds. On the one hand, attention was directed mainly to the role of heating during the stretching process^{11,12}; on the other hand, on the marked dependence of the velocity of molecular rearrangement on the stress,^{13,14} as the cause of the phenomenon itself. The present paper deals with some problems in the theory of cold-drawing. It is superfluous to describe the phenomenon itself. It must only be kept in mind that capability of cold-stretching exist both with crystalline and glass-like polymers in some range of temperatures, which is on one side determined by the temperatures of softening T_g (for the glasslike polymers), and on the other side by the temperature of brittleness. The deformation due to cold-drawing—in contrast to plastic deformation—is thermoreversible, i.e., it vanishes upon heating to a sufficiently high temperature (harring decomposition of material or its transition to liquid state on melting or softening) which is, of course, in connection with the properties of the molecular network of the polymer.

The theory should first give answers to the following questions:

- (1) What is the nature of the experimentally found bend on the constant speed stress-strain curve and of the start of the residual deformation. Further, what determines the value of the critical stress σ_B at which the cold-drawing begins (Fig. 1)?
- (2) Why is there a lowering of σ_B with increasing temperature and an increase of σ_B with increasing stretching speed (Figs. 2, 3, 4)?
- (3) What are the fundamental relations for cold-drawing of both crystalline and glass-like polymers? How do the differences in the structure of both types of materials influence the course of the process?
- (4) What specific properties of the polymer cause the stretching to have a homogeneous ("neckless") or inhomogeneous (with "neck") character (both are found with crystalline and glass-like polymers)? Why does lowering of stretching rate, increase in temperature, and decrease in sample cross section usually lead to a change from inhomogeneous to homogeneous drawing?
- (5) What are the conditions for the relative stabilization of the "neck" (a sharp retardation of its deformation) during inhomogeneous stretching and what determines the value of the "drawing coefficient"?

It is clear that in a short communication it is impossible to give an answer not only to all these questions but even to those which at present can be explained more or less precisely. (The practically important problem of the relation of the properties of the stretched sample to the conditions of stretching is left untouched here.) But formulation of these questions should be helpful in analyzing the present situation in the theoretical field.

Fundamentally, the most important questions are the first three ones. (The more so, as they are pertinent not only to the case of linear deformation, but to any deformation which includes the shear deformation, i.e., in which the form of the sample is changed.)

First it is necessary to clarify the problem of the isothermal and non-isothermal cold-drawing if one is to analyze the different points of views one meets.

In a number of papers^{15,17} attention was mainly directed to the non-isothermal process. It was shown that local heating during stretching can reach several tens of degrees.

Some specific properties of the process were explained (e.g., instability of homogeneous stretching, lowering of the drawing coefficient on increasing the temperature and on lowering the stretching speed, etc.) by taking into account this heating-up, which occurs during the stretching process.

An extreme case is the theory of stepwise softening which attempts to explain the very cause of cold-drawing by this heating-up of the sample. According to this theory, in the area of drawing ("shoulders" at the "neck") the temperature is higher than the softening temperature (of the glass-like polymer), or the melting point (of the crystalline polymer), and the material is actually deformed in a highly elastic state.

The following can be said about the theories of heating and stepwise softening: Both of them treat the non-isothermal stretching which is usually performed in practice, and the determination of the temperature rise in the stretching zone is thus of substantial importance. However, the extent of temperature rise can be lowered by reducing the stretching speed and by improving the heat transfer to the surroundings. Thus the softening effect can easily be excluded, and if the drawing rate is sufficiently lowered, isothermal conditions be attained.

According to approximative calculations, the stretching speed at which heating can be neglected is of the order of 10^{-4} cm./sec. for a sample 2 mm. in diameter in the air. Direct experiments with rubbers in solid state gave for a stretching speed of 10^{-3} cm./sec. the maximal heating-ups of the order of several tenths of degree. Cold-stretching occurs in these as well as in other polymers as before and all its characteristics are preserved. Moreover, in this case a lower stress is required for the beginning of the process than at high elongation speeds. Thus it appears to us that it is most important for the theory to explain in the first place the laws which govern the isothermal cold-stretching, even if we are aware of the importance of the non-isothermal course of cold stretching and of the influence of heat effects in practical conditions. Even in non-isothermal conditions, there is no heating-up at the start of cold drawing, and thus the non-isothermal

69527 Jour Polymer Science - St. II copy 103 - gal 2 - 10 on 12 A-8A by 27 P.
5-22-1958 - 10-BIRD
PROD NO P-167

course of the process does not answer the above-formulated three fundamental questions, and only partially helps answer the last two. (Instability of homogeneous stretching for a number of polymers and neck-formation is also observed under isothermal conditions.) A purely thermodynamic explanation of the phenomenon appears insufficient both because it can be applied only to crystalline polymers (and analogous processes are also observed in glass-like polymers) and because the kinetics of the process is not taken into account. The latter plays a highly important role in cold-drawing.

In the case of vitreous polymers, the treatment of cold-stretching is based on the assumptions of the dependence of relaxation time on stress and of a marked acceleration of relaxation processes under high stress.^{18,19,20} A quantitative expression of these assumptions depends on the choice of an actual polymer model. But even the simplest case with only one relaxation time (highly elastic deformation) and activation energy independent of temperature and linearly decreasing with increasing shear stress enables us to explain the fundamental laws of cold-drawing: the beginning of the process when sufficiently high stresses are attained, the dependence of σ_B on temperature, and the start of cold-drawing are explained in accordance with the relaxation theory as follows. It is assumed that the rate of accumulation of residual deformation (i.e., the rate at which the elastic deformation changes in residual deformation) grows exponentially with the stress and at some moment equals the deformation rate which is given by the operation of the apparatus. The increase in stress stops and further stretching becomes localized in one place as the homogeneous linear elongation is unstable, and a neck is formed (sometimes several necks). If the influence of molecular orientation on the mechanical properties of the polymer is accounted for, even the neck stabilization and some other features of the phenomenon can be explained. Thus, polymers can be divided into two groups: (a) Those whose strength markedly increases upon orientation (an increase in strength in this case is equal to an increase of σ_B with an increase of the residual elongation) which are cold-stretched without necks being formed and (b) those whose increase in strength is relatively small and which form necks on cold-stretching.

Further, if heating-up in the course of stretching is considered, this treatment can be made to include the non-isothermal case. Returning to the case of crystalline polymers, it should be kept in mind that there is less difference between the glass-like and crystalline polymers if the character of the stretching process, the nature of elongation curves, etc. are considered, than there are differences within these two groups. This is seen, for instance if Figures 5 and 6 are compared, as well as both curves of Figure 7. Since the kinetic characteristics of the cold-drawing process for vitreous polymer are known, it was important to compare with them those of the crystalline polymers. The dependence of σ_B on the elongation velocity can be considered as the fundamental proof of the relaxational kinetic of the phenomenon.

Figure 4 shows the data which were obtained by us. These are represented with sufficient precision by the relation (a similar relation follows also from the relaxation theory of the phenomenon)

$$\sigma_B = A + B \log v$$

which is therefore valid for both crystalline and vitreous polymers alike (e.g., for one single polymer—polydimethylsiloxane—in both phases). The difference between both is quantitative only—the values of constant are lower for crystalline polymers. In all cases the stress σ_B at the beginning of cold-stretching is not constant: it is dependent on the elongation speed. These facts give evidence that the laws of cold-stretching for both crystalline and vitreous polymers are similar. This can be explained in the following way: The state of equilibrium for both crystalline and vitreous polymers is the state of orientation, or of elongation if elongating stresses are acting upon the polymer body. This thermodynamic aspect shows the direction of the process. However, in a solid polymer this state of equilibrium cannot be reached if the stresses are small. If the stresses are sufficiently high, the process of transition into an oriented state is markedly accelerated due to the simultaneous action of thermal movement and mechanical stresses. In the glass-like polymer the net formed by intermolecular forces of attraction is destroyed and recreated in a new, oriented form.

Recrystallization takes place in the crystalline polymer in this case. Thus the kinetic treatment maintains the assumption of a special recrystallization of polymers during cold-drawing, which has been confirmed by experiments, and permits us to remove the assumption of a melting point depression to the experimental temperature. Cold-drawing can proceed with final speed even without this condition and the stresses needed are lower, the lower the speed of elongation. It seems possible that in this way the views on crystalline and amorphous polymers can be brought together.

The development of the theory of cold-drawing is now in the stage which less has been done than still has to be done. We can hope that further experimental studies of the kinetics of the phenomenon in isothermal and non-isothermal conditions with simultaneous study of the structural changes, together with the development of the relaxational treatment of the crystalline and amorphous state of polymers, will lead to a theory of cold-drawing which will explain with sufficient clarity not only the general characteristic of this phenomenon, but also its specific difference for glass-like and crystalline states.

Literature

- (1) W. H. Carothers and J. W. Hill, *J. Am. Chem. Soc.*, **54**, 1579 (1932).
- (2) C. W. Bunn and T. C. Alcock, *Trans. Faraday Soc.*, **41**, 317 (1945).
- (3) W. M. D. Bryant, *J. Polymer Sci.*, **2**, 561 (1947).
- (4) R. A. Hoxley and H. A. Nankarrow, *Brit. J. Appl. Phys.*, **2**, 345 (1951).
- (5) V. A. Kargin and T. N. Sogolova, *Z. Fiz. Khim.*, **27**, 1059, 1208, 1215, 1232 (1953); *Doklady Akad. Nauk*, **88**, 967 (1953); *Z. Fiz. Khim.*, **29**, No. 3, 460 (1955).
- (6) A. P. Aleksandrov, *Trudy I. i. II. konf. po vysokomol. soj. S.S.S.R.*, **1945**, 40.
- (7) J. S. Lazurkin and R. L. Fegelson, *Zhur. Tekh. Fiz.*, **21**, 267 (1951).
- (8) J. S. Lazurkin and G. P. Ushakov, *Mechanicheskiye svoystva i fiziki vysokomol. soj.*, **1953**, *Doklady IX. konf. po vysokomol. soj. i fiziki vysokomol. soj.*, **1953**, *Moskva* 1957.
- (9) J. S. Lazurkin, *Mechanicheskiye svoystva polimerov v stikloobraznom sostoyanii*, *Dokl. diss. Moskva* 1954.
- (10) F. H. Müller and K. Jäckel, *Kolloid-Z.*, **129**, 145 (1952).
- (11) I. Marshall and A. B. Thomson, *Proc. Roy. Soc.*, **221**, 541, 1147 (1954); *Nature*, **171**, No. 4340, 1954.
- (12) G. I. Gurevich, *Zhur. Tekh. Fiz.*, **17**, 1491 (1947).
- (13) G. M. Bartenev, *Uspechi khimii*, **24**, 815 (1955).
- (14) J. I. Frenkel, *Kinitsicheskaya teoriya tekuchego, 2nd. Akad. Nauk S.S.S.R.*, **44**, 184 (1945).
- (15) A. Tobolsky, R. E. Powell, and H. Eyring, *Viscous Properties of Matter (The Chemistry of Large Molecules, 1943)*; A. Tobolsky and H. Eyring, *J. Chem. Phys.*, **11**, 125 (1943); H. Eyring and G. Halsey, *Textile Research J.*, **16**, 13, 284 (1946).

Synopsis

Solid polymers—both glass-like and crystalline—can be cold-drawn. In addition to studies of the specific aspects of this process in individual cases, as governed by structural features, the development of a theory of cold-drawing requires an investigation of the general laws of this process. According to the experimental conditions used, cold-drawing may be carried out either isothermally (at low rates of drawing and with good heat dispersion) or non-isothermally. A number of specific features of the non-isothermal process may be explained by a temperature increase in the stressed region; this has in fact been done in published work on this subject. However, the basic features of this phenomenon persist, as has been shown experimentally, in the isothermal cold-drawing of both glass-like and crystalline polymers. These features include: (a) the possibility of cold-drawing, with large residual deformations; (b) the character of the stress-deformation curves; (c) a displacement at the beginning, and a homogeneous or inhomogeneous stretching over the further course of the cold-drawing (both possibilities homogeneous stretching over the further course of the cold-drawing); (d) the effect of being realized in either type of polymer—glass-like or crystalline; (e) the effect of temperature and the rate of drawing v , this dependence being expressed by the relation $\sigma_d = A + B \log v$, valid for both glass-like and crystalline polymers. The values of σ_d depend on the rate of drawing v , this dependence being expressed by the relation $\sigma_d = A + B \log v$, valid for both glass-like and crystalline polymers. The two types differ only in the value of the constant B , which is lower for crystalline polymers (polyethylene, polyamide, crystalline silicone rubber) than for glass-like polymers (polyvinyl chloride, amorphous silicone rubber, polymethyl methacrylate, butadiene-acrylonitrile copolymer, etc.). Crystalline and glass-like polymers differ in their mechanism of cold-drawing. Crystalline polymers, as is well known, undergo recrystallization on deformation; in either type, however, there is a rupture of intermolecular bonds by the effect of drawing, due to the combined effects of thermal motion and mechanical stresses. Hence follows the kinetic, relaxational character of cold-drawing. The dependence of σ_d on the temperature and rate of drawing may be explained on the assumption that the activation energy of the molecular rearrangement is decreased with increasing stresses. Uniform isothermal stretching is, generally speaking, unstable. The fact that it may be realized in practice, and also the stabilization of the block in non-uniform drawing, makes it necessary to assume that the mechanical relaxation properties of the polymer change on orientation.

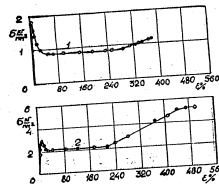


Fig. 7. (1) Elongation curve of a preoriented (100%) polymethyl methacrylate. (2) Elongation curve of a preoriented polyamide (200%). Elongation in $T = 18^\circ\text{C}$. both cases perpendicular to direction of orientation.

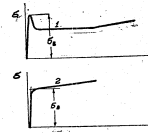


Fig. 1. Schematic presentation of elongation curves. (1) Elongation with "neck". (2) "neckless" elongation.

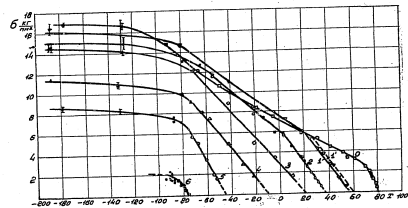


Fig. 2. The dependence of σ_d (open symbols) and brittle strength (closed symbols) on temperature for polyvinyl chloride with various plasticizer content (diethylphthalate, in per cent total weight). (1) Without plasticizer. (2) 9.1%. (3) 16.6%. (4) 23%. (5) 33.4%. (6) 60% (storage for one year).

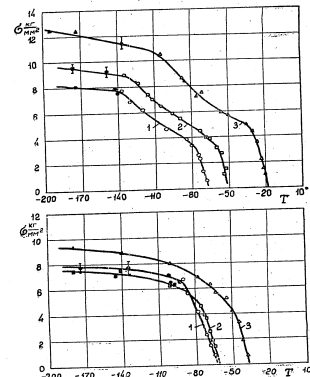


Fig. 3. The dependence of σ_d (open symbols) and brittle strength (closed symbols) for products from various rubbers. Upper part: (1) SKBM; (2) SKS-30; (3) SKN-40; Lower part: (1) butyl rubber; (2) natural rubber; (3) chloroprene.

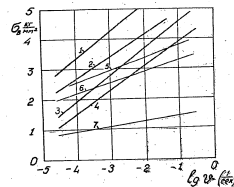


Fig. 4. The dependence of σ_d on elongation speed. (1) Unfilled product from SKN-40; $T = -30^\circ\text{C}$. (2) Unfilled product from silicone rubber in glass-like state; $T = -14^\circ\text{C}$. (3) Plasticized PVC (16.6% diethylphthalate); $T = 22^\circ\text{C}$. (4) Plasticized polymethyl methacrylate (30% dibutylphthalate); $T = 18^\circ\text{C}$. (5) Unfilled silicone rubber in crystalline state; $T = -117^\circ\text{C}$. (6) Oriented polyamide, elongation across the direction of orientation; $T = 20^\circ\text{C}$. (7) Polyethylene; $T = 10^\circ\text{C}$.

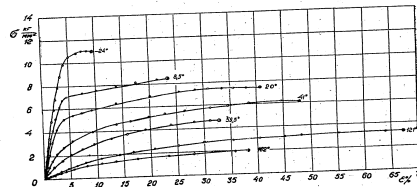


Fig. 5. Elongation curves for crystalline capron. Samples were prepared from a massive isotropic block obtained on cooling the melt with an intermediate exposure at 150°C .

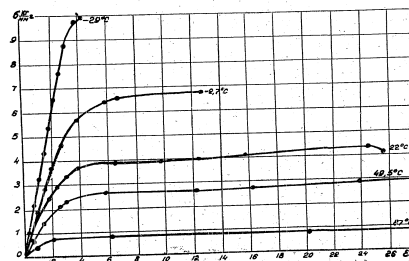


Fig. 6. Elongation curves for celluloid with 20% dibutylphthalate.

Synthesis of Some New Esters and Ethers of Cellulose and Examination of Their Properties

Z. A. ROGOVIN, *The Moscow Textile Institute, Moscow, U.S.S.R.*

In this lecture some basic data about the methods of synthesis of normal esters of cellulose and carbonic and monothiocarbonic acids are given. Comparison of the stability of these esters and esters of cellulose and the dithiocarbonic acid (xanthogenate of cellulose) toward the action of various reagents is given. Further, it is shown that the nature of the acid radical in esters of cellulose and carbonic acid and thiocarbonic acids has a considerable influence on the stability of these esters toward actions of various reagents. The method of synthesis of a new type of cellulose ethers, phenyl ethers of cellulose, was elaborated. Samples of phenylcellulose having a degree of substitution, γ , of 75-80 were prepared, and a preliminary investigation of their properties was carried out.

Among the various types of acid and normal esters of cellulose and carbonic acid and thiocarbonic acid (Table I), until now, only acid esters of cellulose and dithiocarbonic acid (cellulose xanthogenate acid) were examined in detail. These are obtained as the sodium salt of this acid and have a wide field of use as intermediates in the production of viscose fibers and films.

TABLE I
The Composition and Structure of Various Types of Esters of Cellulose and Carbonic and Thiocarbonic acids

Cellulose ester	Structure of cellulose ester	Maximal value obtained up-to-date
Acid ester of cellulose and carbonic acid (Na salt)	$\begin{array}{c} \text{O}-\text{Cel} \\ \parallel \\ \text{C}=\text{O} \\ \parallel \\ \text{O}-\text{Na} \end{array}$	5-10
Normal ester of cellulose and carbonic acid	$\begin{array}{c} \text{O}-\text{Cel} \\ \parallel \\ \text{C}=\text{O} \\ \parallel \\ \text{OR} \end{array}$	75-80
Acid ester of cellulose and monothiocarbonic acid (Na salt)	$\begin{array}{c} \text{O}-\text{Cel} \\ \parallel \\ \text{C}=\text{O} \\ \parallel \\ \text{S}-\text{Na} \end{array}$	100
Normal ester of cellulose and monothiocarbonic acid (Na salt)	$\begin{array}{c} \text{O}-\text{Cel} \\ \parallel \\ \text{C}=\text{S} \\ \parallel \\ \text{S}-\text{Na} \end{array}$	50
Acid ester of cellulose and dithiocarbonic acid (Na salt)	$\begin{array}{c} \text{O}-\text{Cel} \\ \parallel \\ \text{C}=\text{S} \\ \parallel \\ \text{S}-\text{Na} \end{array}$	200-300
Normal ester of cellulose and dithiocarbonic acid	$\begin{array}{c} \text{O}-\text{Cel} \\ \parallel \\ \text{C}=\text{S} \\ \parallel \\ \text{SR} \end{array}$	50-70

Where R is alkyl radical

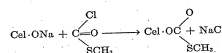
Examination of the conditions of preparation and properties of other compounds of this type, the majority of which has not yet been prepared synthetically, is of considerable scientific interest in studies of the influence of the nature of the acid residue on the properties of the esters prepared. Of practical interest is the study of fundamental possibilities which might lead to new methods of preparation of hydrate cellulose and cellulose ester fibers and films.

In our work we showed that normal cellulose esters of dithiocarbonic acid obtained by the action of solutions of dimethylsulfate, dioxane, monochloroacetic acid, and other reagents on cellulose xanthogenate are considerably more stable to the action of hydrolyzing and saponifying reagents and also to the action of higher temperatures than relatively easily hydrolyzable acid cellulose esters of the same acid. The stability of alkyl or aryl esters of cellulose xanthogenate acid, especially of cellulose methylxanthogenate, to the action of acids and alkalis approaches the stability of acetyl cellulose. But the presence of the group $\text{S}-\text{C}-\text{SNa}$ in this ester considerably decreases its stability toward photochemical action and, thus, the possibility of practical use.

Conditions of preparation of acid esters of cellulose and monothiocarbonic acid by the action of carbon disulfide (COS) on alkali cellulose were examined by Hess and Grotjan,¹ and Philipp.² The acid cellulose ester of monothiocarbonic acid (desthiocarbonic acid) is much less stable, as seen from our experiments, toward the action of saponifying reagents—water and diluted solutions of alkali—than cellulose xanthogenate. In Figure 1 are given data about the relative rate of saponification in ripening of alkaline solutions of cellulose xanthogenate and cellulose desthiocarbonic acid.

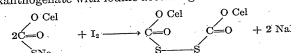
Attempts to prepare normal cellulose esters of monothiocarbonic acid by methods used in synthesis of normal cellulose esters of dithiocarbonic acid gave no positive results. The action of dimethylsulfate, diethylchloroacetamide, monochloroacetic acid, and other reagents on desthiocarbonic acid led to the saponification and decomposition of the latter.

Now we investigate a method of preparation of cellulose methyldesthiocarbonic acid by means of a reaction which we suggested for the synthesis of cellulose methylcarbonates—by the action of methyl monochlorodithiocarbonate on the alcoholate of alkali cellulose according to the following scheme:



Up to now, we have obtained low-substituted esters ($\gamma = 25-30$), which are subject to further investigation.

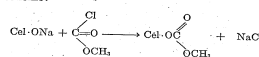
As seen from the investigation, a stable derivative of cellulose desthiocarbonic acid is its disulfide,⁴ which is obtained by the reaction of the solution of desthiocarbonic acid with iodine according to the following scheme:



The experiments performed to compare the stability of the desthiocarbonic acid disulfide and xanthogenate disulfide of cellulose showed that disulfide of desthiocarbonic acid is considerably more stable to the actions of mineral acids, alkalis, boiling water, and also increased temperatures than xanthogenate disulfide of cellulose and also than cellulose acetate. Some experimental data, showing this fact, are given in Figures 2 and 3.

Thus the decrease in the number of atoms of sulfur in the acid residue, which is introduced in the process of esterification into the molecule of the cellulose ester, increases the stability of this ester toward the actions of acids and heating.

This rule displays more clearly in the comparison of properties of normal cellulose or methylcarbonates and methyl dithiocarbonates. Cellulose methylcarbonates having $\gamma = 80-100$ were prepared by the reaction of the methyl ester of carbonyl chloride with the alcoholate of cellulose according to the scheme:



Cellulose alcoholate, which is very reactive, was prepared according to the worked-out method⁶ by an interchange reaction of cellulose with isomyl alcoholate at 70° in xylene solution according to the following equation:



Instead of cellulose alcoholate, alkali cellulose may also be used as starting material.

Cellulose methylcarbonate, as well as cellulose methyldesthiocarbonic acid and methylxanthogenate having a relatively low degree of substitution ($\gamma < 100$), are insoluble in alkalis or other available solvents.

In Figures 5 and 6, data comparing the stability of methylcarbonic and methylthiocarbonic esters of cellulose toward various reagents are given. As seen from these data, the methyl carbonate of cellulose is considerably more stable toward the action of acids than xanthogenate of cellulose. The degree of esterification of the former remains almost unchanged by the action of 1 N H_2SO_4 at 100°C. for six hours, while methylxanthogenate is completely saponified by this treatment.

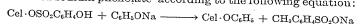
But, in contrast to cellulose methylthiocarbonic acid, cellulose methylcarbonate is very unstable toward the action of diluted alkali. The action of 1 N hydroxide at 25° for five minutes leads to an almost complete splitting off of the ester groups, while the effect of an alkaline solution of the same concentration on methylxanthogenate of cellulose for one hour decreases the degree of esterification only to 20%. Cellulose methylcarbonate is much more stable than cellulose methylxanthogenate toward the action of boiling water: e.g., on boiling cellulose methylcarbonate in water for 5 hours its degree of esterification does not change, while that of cellulose xanthogenate during this period of action falls to 25-30%. If cellulose methylcarbonate is heated in the air for 8 hours at 140°, the degree of esterification does not change while, with cellulose methylxanthogenate, heating under the same conditions reduces the degree of esterification to 20-25%. Therefore, a substitution of the residue of dithiocarbonic acid by a residue of carbonic acid in a normal cellulose ester strongly changes the stability of the resulting esters.

Thus, further technological treatment and the field of application of these esters change correspondingly.

We did not succeed in preparing synthetically an acid cellulose ester of carbonic acid with relatively high γ which would dissolve in a diluted alkali as easily as the acid esters of cellulose with mono- and dithiocarbonic acids. We continue the study of this problem of great practical interest.

Among new types of cellulose ethers, the cellulose phenyl ethers are very interesting. The experiments to prepare these ethers made by various scientists were not successful.

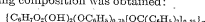
We worked out a method of synthesis of these ethers by means of an interchange reaction of arylsulfonic acids with sodium phenolate. For the preparation of cellulose phenyl ether we use the reaction of the tosyl cellulose ester with sodium phenolate⁷ according to the following equation:



As the cellulose tosyl ether ($\gamma = 100$) dissolves in phenol at increased temperature, this reaction may be carried out in a homogeneous medium, which steps up the rate of alkylation and homogeneity of the prepared cellulose phenyl ether.

Synthesis of the phenyl ether of cellulose is carried out by heating the reaction mixtures for 4 hours at 100°. The phenyl cellulose with $\gamma = 75-80$ obtained is quite soluble in phenol at an increased temperature, and partly soluble in pyridine, cyclohexanone, acetic acid, and quaternary ammonium bases.

To determine the position of phenol groups in the elementary unit of the macromolecule of cellulose, an alkylation of phenyl cellulose by triphenylchloromethane was carried out. The mixture of phenyltrityl ether of cellulose of the following composition was obtained:



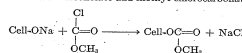
On the basis of these data it is possible to conclude that the phenyl group in the cellulose phenyl ether having $\gamma = 80$, obtained according to our method, contains the phenyl group in position 6.

References

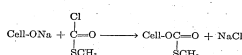
1. Z. A. Rogovin and I. Alexandru, *J. Gen. Chem. U.S.S.R.*, **23**, 7, 1190, 1203 (1953).
2. K. Hess and E. Grotjan, *Z. Elektrochem.*, **56**, 38 (1952); K. Hess, *Reagen. Zellulose*, **31**, 191 (1953).
3. B. Philipp, *Faserforsch. u. Textiltech.*, **6**, 13 (1955); *ibid.*, **6**, 147 (1955); *ibid.*, **6**, 191 (1955).
4. Z. A. Rogovin and M. A. Tuganova, *Khim. Nauka i Prom.*, **2**, 205 (1957).
5. Z. A. Rogovin, Yu. C. Kozlova, and V. A. Derevickaya, *ibid.*, **2**, 264 (1957).
6. Z. A. Rogovin, M. V. Prokofieva, and V. A. Derevickaya, *J. Gen. Chem.*, in press.
7. Z. A. Rogovin, and T. V. Vladimirova, *Khim. Nauka i Prom.*, **2**, 4 (1957).

Synopsis

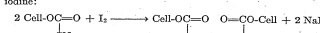
A new method has been devised for the synthesis of triesters of cellulose and carbonic acid by reaction of cellulose alcoholate and methyl chlorocarbonate:



A triester of cellulose with monothiocarbonic acid has been prepared analogously as follows:



A disulfide has been prepared by oxidation of the sodium salt of the thioester with iodine:



A comparison was made of the stabilities toward various reagents of cellulose esters of carbonic, thiocarbonic, and also of the acid and neutral esters of cellulose and monothiocarbonic acid. It was found that the stabilities of the esters toward acids and bases as well as to light and heat vary considerably with the nature of the acid grouping introduced. A method has been worked out for the synthesis of phenyl esters of cellulose by the reaction of sodium phenoxide with *p*-toluenesulfonyl esters of cellulose:



A phenyl ester of cellulose ($\gamma = 70-80$) has been prepared and its properties investigated. It was shown that by this procedure the phenyl group is introduced into position 6.

STAT

STAT

STAT

STAT

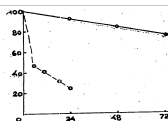


Fig. 1. The relative rate of saponification of xanthogenate and desithioxanthogenate of cellulose in alkaline solutions: (—) cellulose xanthogenate; (---) cellulose desithioxanthogenate. Abscissa: Time, min. Ordinate: Ester groups remaining, % on initial value.

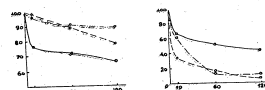


Fig. 2. Stability of desithioxanthogenate disulfide and xanthogenate disulfide towards the action of 2 N H₂SO₄ at 20°C.: (—) xanthogenate disulfide of cellulose; (---) desithioxanthogenate disulfide of cellulose. Abscissa: Time, min. Ordinate: Ester groups remaining, % of initial value.

Fig. 3. Stability of desithioxanthogenate disulfide and xanthogenate disulfide of cellulose towards the action of 2 N NaOH: (—) desithioxanthogenate disulfide of cellulose; (---) xanthogenate disulfide of cellulose; (---) cellulose acetate. Abscissa: Time, min. Ordinate: Ester groups remaining, % of initial value.

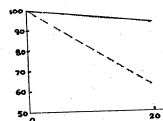


Fig. 4. The change of the degree of esterification, γ , of desithioxanthogenate disulfide and xanthogenate disulfide of cellulose at prolonged heating at 100°C.: (—) desithioxanthogenate disulfide of cellulose; (---) xanthogenate disulfide of cellulose. Abscissa: Time, min. Ordinate: Ester groups remaining, % of initial value.

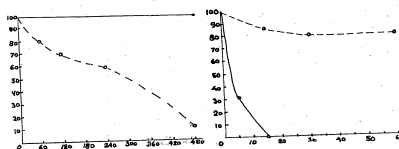


Fig. 5. The stability of cellulose methylcarbonate and methylidithiocarbonate towards the action of 1 N H₂SO₄ at 100°C.: (—) cellulose methylcarbonate; (---) cellulose methylidithiocarbonate. Abscissa: Time, min. Ordinate: Ester groups remaining, % of initial value.

Fig. 6. The stability of cellulose methylcarbonate and methylidithiocarbonate towards the action of 1 N NaOH at 20°C.: (—) cellulose methylcarbonate; (---) cellulose methylidithiocarbonate. Abscissa: Time, min. Ordinate: Ester groups remaining, % of initial value.

69527 Jour Polymer Science - St. II + Formulas - copy 110 gal 1 - 10 on 12
A-SA by 27 P - 5-23-1958 - 13-BIRD
PROD NO P-107

The Effects of Shape in Streaming Birefringence of Polymer Solutions

E. V. FRISMAN and V. N. TSVETKOV, *The Physical Institute of the University of Leningrad, Leningrad, U.S.S.R.*

1. INTRODUCTION

Stream double refraction in polymer solutions is the result of two effects: the intrinsic anisotropy of macromolecules and its shape asymmetry (form effect). The first effect is due to the anisotropic orientation of segments in molecular clusters;¹ the second appears because the distribution of segments in volume of macromolecule has no spherical symmetry about the center of its mass.^{2,3}

The following effects are caused by the form asymmetry: the parabolic dependence of the dynamical constant $[\eta]$ on the refractive index of the solvent,¹⁻⁴ the dependence of value and sign of the relationship $[\eta]/[\eta]$, where $[\eta]$ is the intrinsic viscosity of the solvent, on the molecular weight M of polymer⁵ and, especially, the dependence of the sign of birefringence on the velocity gradient.^{6,7}

All these experimental facts can be explained⁸⁻¹⁰ with use of the model^{11,12} according to which the macromolecule in the solvent is viewed as an ellipsoidal macroscopic particle of which the refractive index, n_m , differs from the refractive index of the solvent, n_s .

The difference between n_m and n_s is

$$n_m^2 - n_s^2 = m/vp (n_1^2 - n_2^2) \quad (1)$$

where n_1 is the refractive index of the polymer in mass, p is the polymer density, m is the mass of a macromolecule, and v is the volume of a macromolecule in solution.

The difference in the two principal polarizabilities of a macromolecule in vacuum is sum of two terms, the first of which gives the intrinsic anisotropy of the cluster,¹ whereas the second represents the anisotropy of its form.¹³

$$\gamma_1 - \gamma_2 = \frac{3}{2} (\alpha_1 - \alpha_2) \frac{h^2}{L^2} + \left(\frac{n_1^2 - n_2^2}{4\pi n_s p N_A} \right)^2 \frac{M^2}{v} (L_2 - L_1) \left(\frac{3}{n_s^2 + 2} \right)^2 = \Theta_1 \frac{h^2}{L^2} + 0.439 (L_2 - L_1) \Theta_2 \quad (2)$$

Here $\alpha_1 - \alpha_2$ is the difference of polarizabilities of segments, h is the distance between the ends of the molecular chain, and L^2 is the mean square of the same value in the absence of deforming forces. $L_2 - L_1$ is a well-known function of the axial ratio p of the macromolecule.

In the range of small velocity gradients ($g \rightarrow 0$), the determination of the mean values of $\gamma_1 - \gamma_2$ for all orientations of macromolecules without considering their deformation leads to the equation for the dynamical constant $[\eta]$ of the solution, which well agrees with the experimental results and has been already discussed.²⁻¹⁰

2. THE THEORY OF FORM EFFECT IN THE REGION OF NON-SMALL GRADIENTS¹⁴

While studying the optical effects of laminar flow in the region of non-small velocity gradients, one must take into consideration the dependence of the asymmetry factor of the macromolecule $L_2 - L_1$ on shearing stress, which can be done in the following manner.

If we take the volume of a molecular cluster under its deformation in the stream as unchanged, the most rational relationship between the asymmetry of the cluster in the stream p and in the absence of the stream p_0 may be the following:

$$p = [1 + \lambda^2(p_0^2 - 1)/\lambda^2]^{1/2} \quad (3)$$

where $\lambda = h/h_0$ and $h_0 = (7/5)^{1/2} \lambda$ is the most probable value of h in the absence of the stream.

If we use the results of the statistical theory of molecular chains,¹⁵ we must take $p_0 = 2$; therefore, equation (3) will then be transformed into equation (3'):

$$p = (1 + \lambda^2)^{1/2} \quad (3')$$

Kuhn's theory¹⁴ gives the distribution of ideally flexible macromolecules (without intrinsic viscosity) in laminar flow:

$$g(h, \theta) = \frac{1}{\pi h_0^2 \sqrt{1 + \beta^2}} e^{-\lambda^2 \left(1 - \frac{\beta}{\sqrt{1 + \beta^2}} \cos 2\theta\right)} \quad (4)$$

Here θ is the angle formed by vector h with the direction of preferential orientation in the flow, β is equal to:

$$\beta = \frac{M}{RT} [\eta] \cdot v_0 \cdot g$$

where v_0 is the viscosity of the solvent, and R and T have their usual sense.

Using equations (2) and (4) with the consideration of (3'), we obtain¹⁴ the following expression for the difference of principal refraction indexes Δn , in a solution of concentration c :

$$\lim_{c \rightarrow 0} \left(\frac{\Delta n}{c} \right) = \frac{3n_s}{4\pi} \left(\frac{3}{n_s^2 + 2} \right)^2 \frac{M}{N_A} = \Theta_1 \beta \sqrt{1 + \beta^2} + \Theta_2 \varphi(\beta) \quad (5)$$

where Θ_1 and Θ_2 are factors characterizing the intrinsic anisotropy of a macromolecule and its form anisotropy; these factors are defined by equation (2).

Parameter $\varphi(\beta)$ is equal to:

$$\varphi(\beta) = - \frac{2\lambda}{1.52\sqrt{1 + \beta^2}} \int_0^\pi e^{-\lambda^2 \left(1 - \frac{\beta}{\sqrt{1 + \beta^2}} \cos 2\theta\right)} J_1 \left(\frac{\lambda \beta}{\sqrt{1 + \beta^2}} \right) \lambda d\lambda \quad (7)$$

where J_1 is Bessel's function of the first order.

For any value of β , the integral in equation (7) may be calculated by the way of numeric integration considering that $L_2 - L_1$ is the function of λ expressed by equation (3'). The function $\varphi(\beta)$ is represented in Figure 1.

The first term of the right side of equation (5) is a well-known result derived by Kuhn,¹⁵ the second one represents the form effect in the dynamic double refraction.

In the region of small values of β ($\beta \leq 2$), equation (6) practically coincides with the result obtained by Gopich¹⁴ in his theory of the form effect in double refraction. Yet, with increasing β , the difference between the two theories becomes more significant; therefore in our theory, factor $\varphi(\beta)$ soon comes near to its asymptotical limit, whereas in Gopich's theory it practically continues to stay proportional to β .

STAT

STAT

69527 Jour Polymer Science - St. II + Formulas - copy 110 gal 2 - 10 on 12
A-8A by 27 P-5-23-1958-14-BIRD
PROD NO P-107

Under our experimental conditions, the solution is not infinitely dilute, and the refractive index of the solvent does not change. However, increasing g produces increases in Θ_i/Θ_s in a given solvent as a consequence of the deformation of macromolecules. This phenomenon brings forth the changes of da/dg which Copic's theory predicts.

The experimental facts discussed here show that the measured value of the orientation angle is not always determined only by the hydrodynamic behavior of solute macromolecules, but that it can also depend on a purely optical factor as the form effect takes place in birefringence. In the case of ideally flexible molecules (the internal viscosity = 0), Copic's theory does not predict similar phenomena. From this point of view, the dependence $\alpha = f(g)$ presented in Figure 5 shows a considerable internal viscosity of the polystyrene macromolecules under investigation ($M = 3.3 \times 10^5$).

For a quantitative comparison of experimental curves for the dependence $\Delta n = f(g)$ (Fig. 4) with those for the theoretical dependence (6), experimental data must be extrapolated to infinitely small concentrations and expressed as a function of the parameter β .

The results for three investigated fractions are represented in Figure 6. Qualitatively, the character of parabolic curves obtained conforms well to equation (6). Quantitative analyses lead to less satisfactory results.

As one can see from equation (6), the initial slope of the curve in Figure 6 gives the sum of values of $\Theta_i + \Theta_s$, whereas the intercept with the β axis (abscissa β_0) permits determination of the relationship

$$\frac{\Theta_i}{\Theta_s} = -\beta_0 \sqrt{1 + \beta_0^2 \varphi(\beta_0)} \quad (10)$$

The values of $\Theta_i + \Theta_s$ obtained from the initial slopes are, in fact, identical to the values determined from equation (8) for the case $g \rightarrow 0$, and, as was shown in section 3, these values are in good agreement with other experimental data.

On the contrary, the relationship Θ_i/Θ_s obtained from (10) turns out to be too great, and the lower the molecular weight of the fraction is, the greater is the discrepancy.

The last circumstance comes directly from the comparison of the curves in Figure 6: the curve for the fraction with $M = 3.3 \times 10^5$ crosses the abscissa much further from the origin than the curve for the fraction with $M = 8.15 \times 10^4$, whereas according to equation (10) the contrary must take place. We may as well say the same about Copic's theory.

It seems that the discrepancy between theory and experiment in the region of great shearing stress, which increases with decreasing molecular weight of the polymer, results in great part from the main failure of our theory, that it does not account for the influence of the internal viscosity of macromolecules. At least, the experimental curves (Fig. 6) show that macromolecules (especially of the low molecular weight fractions) in the flow are less deformable than can be predicted from the distribution function.⁴

5. CONCENTRATION DEPENDENCE OF FLOW BIREFRINGENCE AT LOW SHEAR RATES

As it can be immediately seen from the curves in Figure 4, the concentration dependence of birefringence is very pronounced: with increasing concentration of the solution the Δn versus g curve changes its sign to a negative value at more and more values of g . When limiting our considerations to the region of low shear rates, we obtain for polystyrene in dioxane¹⁰ and butanone the curves $\lim_{g \rightarrow 0} (\Delta n/g) = f(c)$ shown in Figure 7.

Their shape is similar to that of the Δn versus g curves of Figure 4, thus showing the fact that, with increasing concentration of the solution, the relative influence of the shape effect falls abruptly.

It seems probable that this influence of the concentration on the flow birefringence results mainly from two reasons.

The first of them is of a hydrodynamic nature and consists in the increase (at given g) of the shear stress deforming the molecule in the flow with rise in concentration and in the increase of the hydrodynamic interactions of the dissolved macromolecules and a rise in solution viscosity.

The second reason is connected with changes in purely optical properties of the solution when the concentration rises and results only in changes of the form effect, leaving the intrinsic anisotropy effect unaffected. One could call this the "optical interaction" of the dissolved macromolecules.

Indeed, with increasing concentration of dissolved macromolecules and decreasing mean distance between them, the influence of the shape asymmetry of each on its polarizability would decrease, because the mean refractive index of the medium immediately surrounding the molecular coil would be less different from the refractive index of the coil itself.

In other words, at finite concentrations of the solution, the optical polarizability of a given segment will not depend only on the anisotropy of the field created by other segments. One must also take into account the influence of the segments of other macromolecules that are approximately uniformly distributed in the volume of the solvent and thus would level the segment field asymmetry of a given molecule.

The purely hydrodynamic interactions of macromolecules at finite concentrations can be taken into account experimentally by measuring the concentration dependence of birefringence in a solvent with $n_s = n_0$ where the form effect is excluded.

In several papers¹¹ it was shown that, for flexible polymers in solutions where the form effect is absent, the birefringence, $(\Delta n/g)_{g \rightarrow 0}$, rises with the concentration c proportionally to $c\sqrt{n}$, where n_0 is the relative viscosity of the solution. Thus one can obtain the value of the dynamooptical constant $[\eta] = \lim_{c \rightarrow 0} (\Delta n/g)_{g \rightarrow 0}$ from a measurement at finite concentration, substituting the "effective" viscosity of the solution, $\eta\sqrt{n} = \sqrt{\eta_0}$, where η is the solution viscosity for the solvent viscosity.

$$[\eta] = \frac{1}{\sqrt{n_0}} \lim_{c \rightarrow 0} \left(\frac{\Delta n}{g} \right)_{g \rightarrow 0} = \eta^{-1/2} \cdot [\eta]^* \quad (11)$$

$[\eta]^*$ could be called the effective dynamooptical constant at concentration c .

Thus we have equation (12) for calculation of the intrinsic anisotropy Θ_i from data measured at finite concentration and in the absence of the form effect ($\Theta_s = 0$), instead of (8):

$$\frac{[\eta]^*}{[\eta]} \cdot \frac{3n_s kT}{4\pi} \left(\frac{3}{n_s^2 + 2} \right)^2 = \Theta_i \quad (12)$$

The reliability of the empirical formula (11), which is verified for a wide range of experimental data, is demonstrated also in Figure 8, where are shown the values of Θ_i calculated by means of equation (12) from finite

As $[\eta] = \lim_{c \rightarrow 0} \left(\frac{\Delta n}{g} \right)_{g \rightarrow 0}$, then equations (5) and (6) in the region of small values of g when $\beta \rightarrow 0$ give

$$\frac{[\eta]}{[\eta]} \cdot \frac{3n_s kT}{4\pi} \left(\frac{3}{n_s^2 + 2} \right)^2 = \Theta_i + \Theta_s \quad (8)$$

If here Θ_i and Θ_s are inserted from equation (2), bearing in mind that according to the statistical theory¹² the volume v of a macromolecule is, $v = 0.36(kT)^{3/2}$, and the well-known Flory's equation¹³ is used, then one will have

$$\frac{[\eta]}{[\eta]} \cdot \frac{45n_s kT}{4\pi(n_s^2 + 2)^2} = \alpha_1 - \alpha_2 + \frac{2.14}{(\pi n_s N_A n_s)^2} \left(\frac{n_s + n_0}{n_s^2 + 2} \right) (n_s - n_0)^2 \frac{M^2}{v} = \alpha_1 - \alpha_2 + \frac{5.94}{(\pi n_s N_A n_s)^2} \left(\frac{n_s + n_0}{n_s^2 + 2} \right)^2 \frac{\Phi \cdot M}{[\eta]} \quad (9)$$

where Φ is Flory's constant.

Equations (8) and (9) are fully analogous to the equation which may be obtained for $[\eta]$ from the theory of rigid ellipsoids¹⁴⁻¹⁶ with axial ratio $p = 2$.

3. THE FORM IN THE REGION OF SMALL CONCENTRATIONS AND VELOCITY GRADIENTS

The new experimental results obtained in our laboratory while investigating Maxwell's effect in polymer solutions permit a comparison with the results of the above theory.

Equation (9) shows the parabolic dependence of $[\eta]$ on n , which has been observed in many cases in this series of systems.⁴

Figure 2 represents graphically the result obtained for fraction of poly-*p*-tert-butylphenylmethacrylate (*p*-t-BPhMA), molecular weight 6×10^5 which has been investigated in a series of solvents. The use of a large number of solvents has permitted us to find out that the sign of $[\eta]$ is changed twice, with changes of the refractive index of the solvent. Equation (9) shows also that, for the given fraction of polymer (on condition that the values of $n_s - n_0$ are equal), the value $[\eta]/[\eta]$ will be larger in a bad solvent, because the volume of macromolecule v is smaller in this solvent. This conclusion is corroborated experimentally also.^{4,8} Points 12 and 13 presented on Figure 2 may be evident illustration for this conclusion; the first of these (tetrabromoethane) is too high, while the second (monobromonaphthalene) is too low when compared with the other points.

One must take into account that tetrabromoethane is the worst ($[\eta] = 0.36$) solvent, while monobromonaphthalene will be the best ($[\eta] = 1.0$) one for poly-*p*-tert-butylphenylmethacrylate.

Due to equation (9), the dependence of $[\eta]/[\eta]$ on $M/[\eta]$ for fractions of the same polymer in the same solvent must be represented by a straight line, the slope of which will be greater the greater is the ratio $(n_s - n_0)/[\eta]$. The results of measurements carried out with fractions of polystyrene with a wide range of molecular weights (from 5×10^4 to 5×10^5) in three different solvents: bromoform ($n_s - n_0 = 0$), dioxane ($n_s - n_0 = 0.19$), and butanone ($n_s - n_0 = 0.22$) are represented in Figure 3. For each solvent the points fall on a straight line. One must take into account that, in dioxane and butanone, in the region of small molecular weights $[\eta]$ is negative, whereas in the region of large molecular weights, it is positive.

The intercept of each straight line with the ordinate permits the anisotropy of segment to be determined.

As one may see from Figure 3, the segmental anisotropy is almost equal in different solvents: in bromoform, $\alpha_1 - \alpha_2 = -144 \times 10^{-25}$ cm.²; in dioxane, $\alpha_1 - \alpha_2 = -148 \times 10^{-25}$ cm.²; in butanone, $\alpha_1 - \alpha_2 = -152 \times 10^{-25}$ cm.².

The slope of each straight line permits determination of the Flory constant, Φ , the latter, being in full agreement for the two solvents, is, in dioxane $\Phi = 2.35 \times 10^4$; in butanone, $\Phi = 2.40 \times 10^4$.

The study of the form effect in dynamic double refraction of a polymer solution may serve as an independent method for determining the dimensions of its macromolecules, this method being equivalent to another optical one, the method of light scattering asymmetry.

4. DOUBLE REFRACTION IN THE REGION OF LARGE VELOCITY GRADIENTS

Form anisotropy increases with stretching ($\lambda = h/h_0$) of the molecular cluster not so sharply as the intrinsic anisotropy. This fact brings forth a very interesting phenomenon in streaming birefringence of polymer solutions in which the signs of form anisotropy and intrinsic anisotropy are opposite, namely, the change in the sign of stream double refraction of the solution with increasing velocity gradient.

This effect, discovered by E. V. Frisman¹⁷ in solutions of high molecular-weight polystyrene in dioxane, was observed and studied by her further and also in lower molecular-weight fractions of polystyrene in dioxane. The results obtained for the fraction $M = 3.3 \times 10^5$ are given in Figure 4, where the dependence $\Delta n = f(g)$ for solutions of different concentrations is represented. In the region of not too high concentrations, birefringence is positive under small velocity gradients. With increasing g , birefringence reaches the maximum value, then decreases, and changes its sign in the region of velocity gradients where the positive form effect is compensated by the negative effect of intrinsic anisotropy. Measurements of the orientation angle, α , of the optical axis of these same solutions, carried out by E. V. Frisman, have led to discovery of an anomalous dependence, $\alpha = f(g)$. Figure 5 represents the dependence of orientation angle (counted from the flow direction) on the velocity gradient for different concentrations of the polystyrene solutions ($M = 3.3 \times 10^5$) in dioxane. For some concentrations, the orientation angle with increasing g is changed from positive values region to the negative values region. At velocity gradients where the solution birefringence changes in sign ($\Delta n = 0$), the orientation angle changes sharply. In this region of velocity gradients, a very sharp change of sign of the derivative da/dg takes place. da/dg , with increasing g , is changed from negative values to positive ones and then again becomes negative.

We think that the observed dependence of α on g in the velocity gradient region where the negative intrinsic anisotropy is compensated by positive form anisotropy has a direct relation to the theoretical results of Copic's work.¹⁸ Copic has shown that in solutions of macromolecules which have a significant internal viscosity in the solvent in which the absolute value of the negative intrinsic anisotropy Θ_i approaches that of the positive form anisotropy Θ_s , abnormal behavior of the intrinsic orientation number $[\omega] = (da/dg)_{g \rightarrow 0}$ is possible. With a change in the refractive index of the solvent, $[\omega]$ may become equal to zero and may change its sign in as a result of changes in the ratio Θ_i/Θ_s .

STAT

69527 Jour-Poly. Sci., FRISMAN & TSVETKOV KB 110 Gal 4
Prod No P107

concentrations data for several polystyrene fractions in bromoform. For all concentrations and fractions, the points fall within the limits of experimental error, near the same value, $\Theta_1 = -57 \times 10^{-28} \text{ cm}^2$.

It should be pointed out, moreover, that the scatter of values for a given fraction is far less than for a given concentration but different fractions.

Recently, Peterlin¹⁰ proposed another empirical formula that takes into account the concentration dependence of the Maxwell effect and according to which the multiplier $[\eta]^2/[\eta] \cdot \eta^2$ in equation (12) must be replaced by $[\eta]^2/[\eta]^2$, where $[\eta]^2 = (\eta - 1)/c$. For polymers of mean and low molecular weight, Peterlin's formula is equivalent to ours, but for high molecular weight specimens its accord with experiment is somewhat less.

6. THE CONCENTRATION DEPENDENCE OF FORM ANTISOTROPY

When the birefringence of a solution of finite concentration is studied in a solvent allowing the shape effect, then, according to the preceding section, equation (8) must be replaced by

$$\frac{[\eta]^2}{[\eta] \cdot \eta^2} \frac{3n_0 kT}{4\pi} \left(\frac{3}{n_0^2 + 2} \right)^2 = \Theta_1 + \Theta_2^* \quad (13)$$

where Θ_2^* is the effective form anisotropy of the macromolecules in a solution of a given concentration. Θ_2^* differs from Θ_2 , the form anisotropy at infinite dilution because of the already mentioned optical interaction of the macromolecules.

The substitution of the experimental values of $[\eta]^2$, $[\eta]$ and $\sqrt{\eta}$ for a polymer fraction into equation (13) permits calculation of the sum $\Theta_1 + \Theta_2^*$ for this fraction in a given solvent at a fixed concentration. Though Θ_1 does not depend on the molecular weight, the solvent (cf. Fig. 3), or the concentration, the extraction of Θ_1 from the mentioned sum gives Θ_2^* . The values of Θ_2^* obtained thus for a fraction of poly-*p*-tert-butylphenylmethacrylate with $M = 6 \times 10^5$ in several solvents are plotted in Figure 9 as functions of the concentration.

Figure 10 represents the concentration dependence of the ratios Θ_2^*/Θ_1 obtained for several fractions of polystyrene in dioxane and butanone (from the experimental data of Figure 7).

The observed decrease of the effective form anisotropy with increasing concentration can be estimated by means of the following general considerations.

The expression for Θ_2 , which is determined by the second member of equation (2) is obtained from formula (1) which gives the difference between the refractive indices of the macromolecule n_m and the surrounding medium (n_s) in an infinitely dilute solution.

In a solution of finite concentration c (in g./cc.), the effective refractive index of the surrounding medium, n_s^* , obviously differs from n_s , having a value somewhat between n_s and n_m .

The mean macroscopic dielectric constant of the solution, ϵ , is obviously:

$$\epsilon = \epsilon_s \left(1 - \frac{vc}{m} \right) + \epsilon_m \frac{vc}{m}$$

because vc/m is the fraction of volume occupied by the molecular coils. Accordingly, the square of the mean macroscopic refractive index of the solution is:

$$n_s^2 = n_s^2 + (n_m^2 - n_s^2) \frac{vc}{m} \quad (14)$$

The most rough approximation would be to set n_s^* equal to n_s . But in such a case at a volume concentration $vc/m = 1$, when the molecular coils are filling the entire volume of the solution, n_s^* as follows from (14), would equal n_m , and the shape effect should be absent. In reality, however, the mass distribution within a coil is not uniform, and its density decreases from the center to the periphery; it follows that the asymmetry of the field of the segments within the coil, which gives rise to the shape effect, must remain even when the equivalent molecular ellipsoids are "in contact." In other words, n_s^* cannot be equal to n_s , and n_s^* must differ from n_s more than n_s .

By analogy with equation (14) it is natural to assume that

$$(n_s^*)^2 = n_s^2 + (n_m^2 - n_s^2) \cdot F(vc/m) \quad (15)$$

where $F(vc/m)$ is an unknown function of the volume concentration of the molecular coils in the solution.

Thus the effective difference of the refractive index of the coil n_m and the surrounding medium n_s^* will be

$$n_m - n_s^* = n_m^2 - n_s^2 = (n_m^2 - n_s^2) [1 - F(vc/m)] \quad (16)$$

then it follows that

$$\Theta = \Theta_1 [1 - F(vc/m)]^2 \quad (17)$$

where $v = (0.36/\phi) [\eta] \cdot M$, $vc/m = (0.36/\phi) \cdot N_A \cdot [\eta] \cdot c \approx [\eta] \cdot c$. Expanding the function F into series one can write:

$$\Theta = \Theta_1 (1 - k_1 [\eta] \cdot c + k_2 [\eta]^2 c^2 + \dots) \quad (18)$$

where k_1 and k_2 are interaction coefficients. Equation (18) must be compared with experimental curves (Figures 9 and 10).

It follows from (18) that the relative initial slopes of the curves in Figures 9 and 10 must be proportional to the intrinsic viscosities of the corresponding polymer-solvent systems:

$$-\frac{1}{\Theta_1} \left(\frac{d\Theta}{dc} \right) = k_1 \cdot [\eta] \quad (19)$$

The feasibility of equation (19) for all explored systems is shown in Figures 11 and 12 where the relative initial slopes of Figures 9 and 10 are plotted against the intrinsic viscosity of the corresponding systems. It can be seen that for either a given polymer in different solvents (Fig. 11) or for fractions of another polymer differing in their molecular weights by a factor of 50 (Fig. 12), the points fall on straight lines, with slopes giving $K_1 = 0.40$ for *p*-*t*-BPhMA and $K_1 = 0.38$ for polystyrene.

Thus equation (18) — at least in the region of moderate-high concentrations — proves to be enough universal. It is interesting to point out that the interaction constant of the macromolecules, K_1 , approaches the hydrodynamic constant K' in the well-known Huggins' equation.

In this paper, in addition to data from the sources cited in the references, some experimental results obtained by fellows of the laboratory I. N. Shtemkova, T. I. Garmenova, and V. E. Bychkova, were also used.

The authors are indebted to Dr. O. B. Ptitsyn for a fruitful discussion of some problems mentioned above.

69527 Jour Polymer Science - St. II + Formulas - copy 110 gal 5 - 10 on 12
A-SA by 27 P - 5-24-1958 - 3-BIRD,
PROD NO P-107

References

1. W. Kuhn and F. Grun, *Kolloid-Z.*, **101**, 247 (1942).
2. V. N. Tsvetkov and A. I. Petrova, *Zhur. Tekh. Fiz.*, **14**, 289 (1944); *Rubber, Chem. and Technol.*, **19**, 360 (1946).
3. V. N. Tsvetkov and E. V. Frisman, *Acta Physicochim. U.R.S.S.*, **20**, 61, 363, (1945).
4. V. N. Tsvetkov, E. V. Frisman, and L. S. Muchina, *Zhur. Ekspit. Teoret. Fiz.*, **30**, 449 (1956).
5. E. V. Frisman and V. N. Tsvetkov, *Zhur. Tekh. Fiz.*, **25**, 447 (1955).
6. E. V. Frisman and V. N. Tsvetkov, *Doklady Akad. Nauk S.S.S.R.*, **106**, 42 (1956).
7. V. N. Tsvetkov, *Chem. listy*, **49**, 1419 (1955).
8. V. N. Tsvetkov, *J. Polymer Sci.*, **23**, 151 (1957).
9. V. N. Tsvetkov, *Simpósio Internazionale di Chimica Macromolecolare*, Torino, 1954. Published in *Ricerca sci.*, **25**, 413 (1955). Distributed in the U.S. by Interscience, N. Y.
10. V. N. Tsvetkov and E. V. Frisman, *Doklady Akad. Nauk S.S.S.R.*, **97**, 647 (1954).
11. V. N. Tsvetkov, E. V. Frisman, O. B. Ptitsyn, and S. I. Kotljars, *Zhur. Tekh. Fiz.*, **1957**, in press.
12. H. Kuhn, *Experientia*, **1**, 28 (1945). *Helv. Chim. Acta*, **31**, 1677 (1948).
13. W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **26**, 1395 (1943); **28**, 1533 (1945).
14. M. Copik, *J. Polymer Sci.*, **20**, 593 (1956).
15. W. Kuhn and P. Buchner, *Ergeb. Exakt. Naturw.*, **25**, 67 (1951).
16. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ., 1953.
17. M. Copik, 1957, in press.
18. E. V. Frisman and E. N. Arshipova, *Doklady Akad. Nauk S.S.S.R.*, 1957, in press.
19. A. Peterlin, *Bl. Acad. yougosl.*, **1**, 39 (1953).

Synopsis

In this paper are presented new results obtained during further experimental and theoretical investigations of the form effect in the dynamic double refraction of polymers in solution. The use of the dumbbell theory of W. Kuhn for flexible chains in solution and of the optical model of an equivalent ellipsoid for the macromolecule, permits the formulation of a theory of flow birefringence which takes account of the form effect for a wide range of shear rates. The conclusions of this theory are compared with new experimental data obtained in a study of polystyrene and *p*-*tert*-butylphenylmethacrylate in different solvents. In the range of low shear rates and concentrations, the theory is found to be in a good accord with experimental results. On the contrary, the study of the double refraction of several polystyrene fractions in dioxane in a wide range of shear rates and concentrations shows that macromolecules are less deformable in the flow than it follows from the dumbbell theory for ideally flexible chains. A new phenomenon was discovered experimentally—an anomalous dependence of the orientation angle on the shear rate of flow in the range of shear stresses at which the birefringence changes its sign because of compensation of the positive shape effect by the negative intrinsic anisotropy effect. Investigation of the concentration dependence of flow birefringence shows that this dependence is due to two causes—the hydrodynamic and optical interaction of the molecules. The optical interaction is characteristic only for those solutions in which the form effect takes place. A simple theory of concentration dependence of the form effect is proposed which is in good accordance with experimental data.

Discussion

A. Peterlin (*Ugubana*): I must congratulate Prof. Tsvetkov on the many new results on streaming birefringence and on its dependence on concentration and gradient he was able to obtain. Since the behavior of the orientation angle cannot be explained by the model of the soft molecule, I would like to ask Prof. Tsvetkov whether the results can be located between the limits of the soft coil and the rigid ellipsoid. The calculations for both limits were made some time ago by Copik and Kuhn. In that case, the experiments can probably be interpreted by the model of the semi-rigid coil, may be in terms of the theory presented by Cerf. When, however, the experiments are not between these limits, the situation is more complicated and would require a further extension of the theory.

The disagreement between theory and experiment is also partly due to the polydispersity of the samples which influences the streaming birefringence and the orientation angle in a completely different way as was shown a very long time ago by the investigations of Sadron.

V. N. Tsvetkov (*Levinograd*): The anomalous behavior of the orientation angle, observed and described by us, is specific only for solutions, in which the shape effect equals in magnitude and differs in sign from the intrinsic anisotropy effect.

Since we remain within the limits of Kuhn's dumbbell theory corrected for the shape effect by Copik and the present authors, one can conclude that one deals with an intermediate case of half-rigid coils. Indeed, for fully soft molecules the above mentioned behavior of the orientation angle cannot take place, for, as Copik has shown, for such molecules the presence of the shape effect does not change the course of the orientation angle. On the other hand, the macromolecules investigated by us cannot be absolutely rigid, because their deformation in flow is quite obvious, appearing as the reversal of the sign of birefringence with increasing shear rates (the Frisman effect).

The quantitative disagreement between the theoretical values of streaming birefringence for absolutely soft molecules [equations (6) and (10)] and the experimental data obtained for fractions of various molecular weight can be understood in terms of Kuhn's theory, if one assumes that the molecules under study are half-rigid, and that the degree of their rigidity (internal viscosity) diminishes with augmenting molecular weight.

It is difficult to say whether one can interpret the foregoing phenomena in terms of Cerf's theory, for in it the different dependence of the intrinsic anisotropy and shape effects on the shear rate is not taken into account.

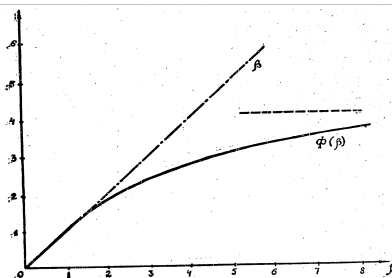
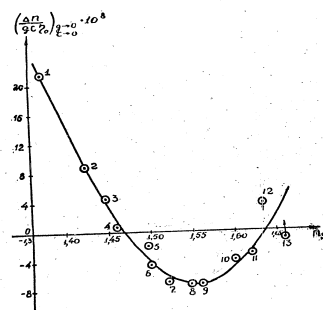
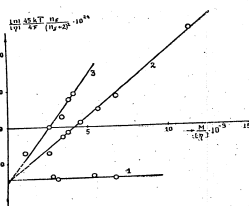
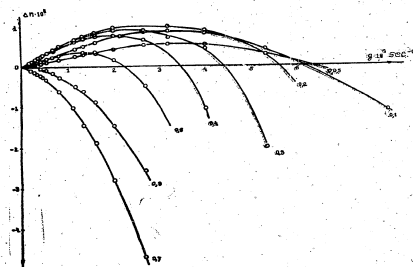
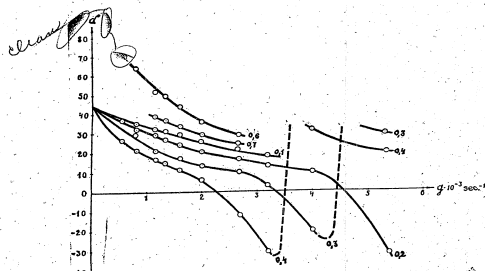
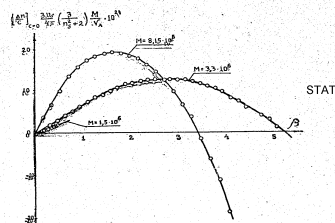
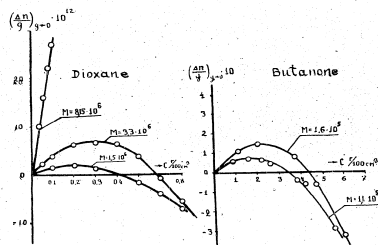
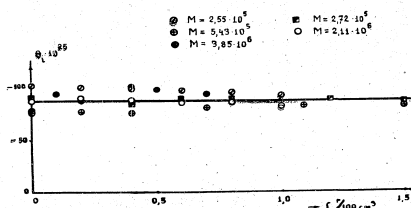
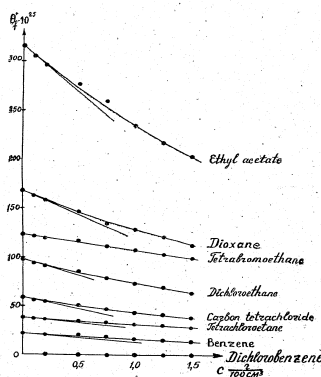
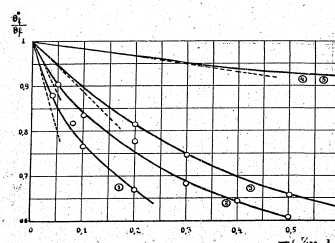
Fig. 1. Dependence of $\phi(\beta)$ on β .Fig. 2. Relation between dynamical constant $[\eta]$ and refractive index of solvents for poly-p-tert-butylphenylmethacrylate.Fig. 3. Relation between ratio $[\eta]/[\eta]_0$ and ratio $M/[M]_0$ for polystyrene in three solvents. 1. Bromoform: $\alpha_1 - \alpha_2 = -144 \times 10^{-28} \text{ cm}^2$; 2. Dioxane: $\alpha_1 - \alpha_2 = -145 \times 10^{-28} \text{ cm}^2$; $\phi = 2.35 \times 10^{21}$; 3. Butanone: $\alpha_1 - \alpha_2 = -152 \times 10^{-28} \text{ cm}^2$; $\phi = 2.40 \times 10^{21}$.Fig. 4. Relation between double refraction of flow, Δn , and velocity gradients, g , for polystyrene ($M = 3.3 \times 10^5$) in dioxane. The numerals at the curves indicate the concentrations in $\text{g}/100 \text{ cm}^3$.Fig. 5. Relation between orientation angles, α , and velocity gradients, g , for polystyrene ($M = 3.3 \times 10^5$) in dioxane. The numerals at the curves indicate the concentrations in $\text{g}/100 \text{ cm}^3$.Fig. 6. Relationship between flow birefringence $(\Delta n/c)_0 \rightarrow \infty$ of infinitely dilute solutions and the orientation parameter $\beta = (M/RT) \cdot [\eta] \cdot g$ for polystyrene fractions.Fig. 7. Relation between flow birefringence in region of small velocity gradients $(\Delta n/c)_0 \rightarrow \infty$ and concentration for fractions of polystyrene in dioxane and butanone.

Fig. 8. Intrinsic anisotropy of macromolecules of polystyrene in solutions of different concentrations. Solvent, bromoform.

Fig. 9. Relation between form anisotropy θ^* of macromolecules and concentration C for poly-p-tert-butylphenylmethacrylate in various solvents.Fig. 10. Relation between relative form anisotropy, θ^*/θ , and concentration for solutions of polystyrene fractions. (1) $M = 8.15 \times 10^4$ in dioxane; (2) $M = 3.3 \times 10^5$ in dioxane; (3) $M = 1.5 \times 10^6$ in dioxane; (4) $M = 1.6 \times 10^6$ in butanone; and (5) $M = 1.1 \times 10^6$ in butanone.

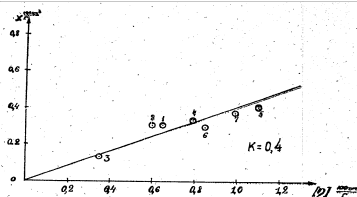


Fig. 11. Relation between initial slopes of the concentration dependence of the form anisotropy, $\frac{1}{\delta} \left(\frac{d\delta}{dc} \right)_{c=0}$, and intrinsic viscosity of solutions, $[\eta]$, for poly-*p*-tert-butyl-phenylmethacrylate in various solvents ($M_f = 6 \times 10^5$): (1) ethyl acetate; (2) dioxane; (3) tetrabromethane; (4) dichloroethane; (5) carbon tetrachloride; (6) tetrachloroethane; and (7) benzene.

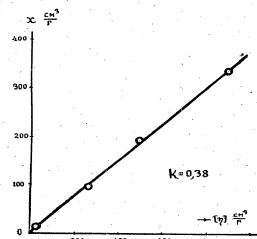


Fig. 12. Relation between initial slopes of the concentration dependence of the form anisotropy, $\left(\frac{1}{\delta} \frac{d\delta}{dc} \right)_{c=0}$, and intrinsic viscosity of solutions $[\eta]$ for polystyrene fractions in butanone and dioxane.

Mutual Solubility of Polymers and Properties of Their Mixtures

G. L. SLONIMSKIĬ, *Chemical Science Section, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.*

I. INTRODUCTION

If a homogeneous mixture of two polymers is to be obtained, both components must exhibit fluidity. It is, therefore, necessary first of all to analyze the process of mixing of two amorphous linear polymers capable of developing true irreversible deformation. However, though the mixing of two such polymers, from the thermodynamic point of view, constitutes the mutual solution of two liquid phases, it does not, in fact, take place spontaneously, since the exceptionally high viscosity of polymers results in a negligible rate of diffusion of the long-chain molecules (mixed milling, evaporation of solvent from mixed solutions, etc.) are used to obtain polymer mixtures which exhibit no heterogeneity, even when examined by means of a good optical microscope.

It is, however, quite evident that, should two polymers be mutually insoluble, the spontaneous separation of such artificially prepared mixtures into macroscopically distinct phases must proceed at infinitesimal rates as a result of the enormous viscosity of the system. In such cases, the flexibility of the chain, which permits the relatively rapid translations of individual segments of the chain, is an important factor. This property of chain molecules will result in a process by which the mixture of mutually insoluble polymers becomes resolved in extremely small volume elements, i.e., to the formation of two types of regions whose composition will accord with the thermodynamic conditions of phase separations.¹⁻⁴ Such mixtures of two amorphous polymers structurally closely resemble crystalline polymers, which are also microheterogeneous. In both cases, the dimensions of the regions differing in phase character formed by the segregation of segments are considerably smaller than the length of the chain molecules.

For this reason, the macroscopic miscibility of two polymers is by no means equivalent to their microscopic miscibility, i.e., to true mutual solubility of the polymers.

In connection with the two different possibilities of mixing, the problem arises of the effect of the nature of mixing on the physical properties of true mixtures. In addition, it is necessary to determine in which cases true mutual solubility of two polymers may be expected. According to current theory, the mutual solubility of two polymers is determined almost entirely by the sign of the heat of mixing.⁴⁻⁶ Since it may be anticipated that, in the large majority of cases, the mixing of two polymers be endothermic, true mutual solubility of polymers should be rare. In fact, the mixing of two polymers (in the same solvent) has been shown,^{7,8} as a rule, to lead to the separation of two layers, i.e., two phases. It seemed important to determine experimentally the heats of mixing of various polymers and to confront the values found with the properties of mixtures of these polymers and the behavior of mixtures of their solutions.

II. EXPERIMENTAL

Direct measurement of the heat of mixing of two polymers is practically impossible because of the high viscosity of such systems. However, its value may be determined with the aid of Hess's law of the independence of heat effects on the particular path chosen. Thus, for instance, by measuring the heat Q_1^* evolved when 1 gram of pure polymer A and 1 gram of pure polymer B are dissolved together in a large volume of solvent, and the heat Q_2^* evolved when 2 grams of a macroscopically homogeneous 1:1 mixture of polymers A and B is dissolved in the same amount of solvent, we may determine the integral heat of mixing Q_m per unit weight of polymers A and B.

$$Q_m = Q_1^* - Q_2^*$$

The author (together with G. V. Struminskii) has carried out detailed determinations of the heats of solution of various polymers and their mixtures.^{9,10} From the results obtained, the integral heats of mixing were calculated according to the formula:

$$Q_m = Q_1 + Q_2 + Q_3 - Q_4$$

where Q_1 and Q_2 are the heats of solution per gram of polymers A and B, respectively, in 100 grams of the pure solvent, Q_3 is the heat of mixing of these solutions of polymers A and B, and Q_4 is the heat of solution of a mixture containing 1 gram of polymer A and 1 gram of polymer B in 200 grams of the pure solvent.

TABLE I
Intrinsic Viscosities of Polymer Solutions

Polymer	Abbreviated name	Solvent	Intrinsic viscosity
Sodium butadiene rubber	SKB ^a	Benzene	1.70
Butadiene-styrene rubber	SKS-30	"	1.50
Natural rubber	NK	"	3.40
Nitrocellulose (11.9% N)	N. Cell	Acetone	1.90
Cellulose acetate (ac. gr. 50%)	Ac. cell (50%)	"	2.00
Cellulose acetate (ac. gr. 45%)	Ac. Cell (45%)	"	1.25
Benzylcellulose	B. Cell	Chloroform	1.40
Polystyrene ^a	PS ^a	Benzene	2.90
Polystyrene ^b	PS ^b	"	"
Polyvinylacetate ^a	PVAc ^a	Acetone	1.77
Polyvinylacetate ^b	PVAc ^b	"	1.02
Polyacrylonitrile	PMA	"	3.20
Polybutylacrylate	PBA	"	1.00
Polyethylmethacrylate	PME	"	1.30
Polybutylmethacrylate	PBM	"	5.10

^a The superscripts refer to the polymer batch number.

^b Molecular weight 22,400.

Table I characterizes the polymers used; Table II records the experimental heat values obtained; and Table III shows the behavior of solutions of pairs of polymer in the same solvent on mixing.

As may be seen from these data, in all cases where the mixing of the polymers is endothermic, mixtures of their solutions separate into two phases. However, when the process is exothermic, the two solutions do not always form a single phase as would be expected on the basis of current theory.¹ The systems anomalous in this respect are a polybutadiene-butadiene-styrene copolymer (30% styrene) and polybutadiene-polystyrene these systems will be considered later.

69527 Jour Polymer Science - St. H + Formulas - copy 114 gal 3-10 on 12.
A-8A by 27 P-5-26-1958-9-BIRD
PROD NO P-41

TABLE II
Integral Heat of Mixing of Polymers

Polymer	Heat of solution of polymer Q_s , cal./g.	Polymer	Heat of solution of polymer Q_s , cal./g.	Common solvent for both polymers	Heat of mixing of polymer solutions, cal./2 g.	Heat of mixing of polymer solutions, cal./2 g.
SKB ¹	-1.55	SKS-30	-0.73	Benzene	0	-2.75 ± 0.5
SKB ²	-1.73	PS ¹	+6.55	"	0	+4.50 ± 0.3
SKB ³	-1.73	PS ²	+5.47	"	0	+3.18 ± 0.6
SKB ⁴	-1.66	Ethylbenzene	-1.08	"	0	-4.26 ± 0.3
NK	-2.38	SKB ¹	-1.55	"	0	-2.85 ± 0.3
NK	-2.38	SKS-30	-0.73	"	0	+11.60 ± 1.3
B. cell	+3.47	PS ¹	+6.58	Cyclohexane	0	+11.60 ± 1.3
B. cell	+8.95	PS ²	+3.90	Chloroform	0	+18.78 ± 3.9
N. cell	+18.78	Ac. cell (56%)	+10.65	Acetone	0	+23.56 ± 5.9
N. cell	+18.78	PVAc ¹	+0.68	"	-0.25	+18.90 ± 0.9
Ac. cell (56%)	+10.65	PVAc ²	+0.68	"	0	+14.24 ± 2.9
Ac. cell (56%)	+10.65	Ac. cell (48%)	+8.46	"	-0.36	+26.70 ± 8.0
PMA	0	PBM	-2.44	"	-0.66	-3.13 ± 0
PMA	0	PM	+7.12	"	-0.40	+9.26 ± 2.5
PMA	0	PM	-2.44	"	-0.40	-2.07 ± 0.6
PBA	0	PM	-2.44	"	-0.25	+4.78 ± 0.3
PM	+7.18	PM	-2.44	"	-0.24	+2.57 ± 1.0
PVAc ¹	+0.18	PM	+1.62	"	-0.24	+2.57 ± 1.0
PVAc ²	+0.68	PBA	-0.2	"	-0.55	+0.39 ± 0.4

TABLE III
Behavior of a Polymer Mixture in a Common Solvent

Mixed solution of polymers	Solvent	Behavior of the solution mixture
SKB + SKS-30	Benzene	Separates into two phases
SKB + SKS-30	Gasoline	"
SKB + PS ¹	Benzene	"
SKB + PS ²	"	"
SKB + ethylbenzene	"	Remains homogeneous
NK + SKS-30	"	Separates into two phases
NK + SKB	"	Remains homogeneous
NK + PS ¹	Cyclohexanone	Separates into two phases
B. cell + PS ¹	Chloroform	"
N. cell + Ac. cell (56%)	Acetone	Remains homogeneous
Ac. cell (56%) + Ac. cell (48%)	"	Separates into two phases
Ac. cell (56%) + PVAc ¹	"	"
PMA + PBM	"	"
PMA + PM	"	"
PM + PM	"	"
PM + PVAc ¹	"	"
PM + Ac. cell (56%)	"	"
PVAc ¹ + PBA	"	"
Ac. cell (48%) + PVAc ²	"	"
PBA + PM	"	"

To determine the effect of mutual solubility on the properties of polymer mixtures, the author (together with N. F. Komsikina) has investigated the properties of raw rubber stocks prepared from the mixture of two rubbers, of unvulcanized combined rubbers.¹⁰ The behavior on mixing of solutions of the polymers was also examined. The following materials were used: natural rubber (NK), sodium-butadiene rubber (SKB), butadiene-styrene copolymers with varying amounts of styrene (SKS-30 and SKS-10), and a butadiene-acrylonitrile rubber (SKN-18). Typical rubber stocks with 50 parts by weight of carbon black per 100 parts of polymer or polymer mixture and a vulcanizing additive containing sulfur and mercaptobenzothiazole were used. Special attention was paid to uniform distribution of the ingredients in the rubbers and thorough kneading of the rubbers. The unvulcanized rubber stocks or rubbers obtained were subjected to standard tests as well as to certain additional laboratory investigations.

The measurements showed that the dependence of a number of mechanical properties of the rubber stocks and rubbers on the ratio of the component polymers in the mixture showed well-defined extremes in the case of the combinations of butadiene-acrylonitrile copolymer (SKN-18) with polybutadiene (SKB) or the butadiene-styrene copolymer (SKS-30), and also the combination SKB + SKS-30, the system polybutadiene-natural rubber exhibited a monotonic change in properties. By way of example, Figures 1, 2, and 3 record the findings for certain mechanical properties of rubbers prepared from mixtures of polybutadiene with butadiene-acrylonitrile copolymer (SKB + SKN-18) or a butadiene-styrene copolymer (SKB + SKS-30) and of natural rubber with butadiene rubber (NK + SKB). Similar phenomena are observed in the case of other mechanical properties. Thus, e.g., with a change in the ratio of the components, the mechanical losses of the rubbers, shown in Figures 1 and 2, pass through maxima, while endurance to multiple bending passes through minima (Fig. 4).

Investigation of the viscosity (at 100°C.) of the raw rubber mixtures and of the unvulcanized rubber stocks showed that this property, too, passes through a maximum with respect to dependence on the composition of the mixture for those cases in which the corresponding combined rubbers exhibit the extremes mentioned above. However, in the system butadiene rubber (SKB)-natural rubber (NK), the viscosity-composition curve shows a monotonic character. For example, the appropriate curves for four combined mixtures of raw rubbers and the corresponding unvulcanized rubber stocks are shown in Figures 5 and 6.

Since most of this work was carried out with combined rubber and not with mixtures of pure raw rubbers, it was necessary to verify the effect of the additives, particularly the filler, vulcanizing additive, and plasticizer. The investigation showed that the presence or absence of extremes on the property versus composition curves was determined solely by the polymers themselves, though the values and positions of the maxima or minima might be affected to some extent.¹¹

III. DISCUSSION

The investigation of mechanical properties described above showed that raw rubber mixtures, mixed rubber stocks, and rubbers prepared from mixtures of two raw rubbers fall into two groups: one includes those systems in which the dependence of various properties on the ratio of the polymeric components is high; the other includes systems which show monotonic changes in properties. Since the first group includes systems such as mixtures of the polar butadiene-acrylonitrile copolymer, SKN-18

with the non-polar butadiene, butadiene-styrene, and natural rubbers, and the second mixtures of two non-polar rubbers, polybutadiene (SKB) and natural rubber (NK), it seems evident that the systems of the first group are microheterogeneous (as a result of phase separation in micro-regions), while systems of the second group represent true polymer-in-polymer solutions. The behavior of solutions of the corresponding pairs of polymers on mixing fully confirms this assumption.

In this connection, particular interest attaches to the systems polybutadiene-butadiene-styrene copolymer (SKB-SKS-30) and polybutadiene-styrene copolymer (SKB-PS), which, as has been mentioned, show distinct extremes in the property-composition curves (cf. Figs. 2, 4, and 5) and phase separation, when mixed in solution, but nevertheless exhibit an exothermal effect on mixing (cf. Table II). This behavior, though at first sight incompatible with the general theoretical view, can be readily understood on more detailed analysis.

It is evident that, since a mixture of solutions of SKB and SKS-30 separates into two phases, the mixing of these solutions requires the absorption of heat (though the absolute value of the effect may be small). The extremes on the property-composition curves of the corresponding rubbers, tremes on the property-composition curves of the corresponding rubbers, show equally clearly that, in the course of preparation of these rubbers, separation of the system into two phases in microregions occurred, this separation being fixed by vulcanization. Hence, at the temperature of formation of the rubber (143°C.), the mixing of the two polymers must also be endothermic. Since the copolymer SKS-30 contains phenyl groups but the polybutadiene SKB does not, the endothermic effect of mixing the two raw rubbers is in accordance with the known endothermic effect observed on mixing low-molecular aromatic and aliphatic liquid hydrocarbons (e.g., benzene and hexane) and with the absorption of heat observed when SKB is dissolved in ethylbenzene (cf. Table II), a simple low-molecular model of polystyrene. It follows, therefore, that the exothermic effects observed by us for the mixing of polybutadiene with SKS-30 or with polystyrene at room temperature are due not to intermolecular interactions, which are the same for polystyrene and for ethylbenzene, on the one hand, and of ethylbenzene, on the other. These differences have recently been revealed in a number of papers¹²⁻¹⁴ in which it was shown that polymers possessing relatively rigid chain molecules have lower densities than should have been expected on the basis of the values for the hydrogenated monomers and the monomers themselves with the contraction on polymerization being taken into account. For polystyrene, in particular, it was demonstrated that the release of heat observed when this polymer is dissolved in ethylbenzene is due to the loose arrangement of the polystyrene molecules at room temperature. It was also shown that butadiene-styrene copolymers retain the loose structure typical of polystyrene to an extent dependent on their styrene content.¹⁵

The release of heat on mixing SKS-30 or polystyrene with polybutadiene, is hence, due to a decrease in the total volume of these systems on mixing. However, at temperatures above the softening-point of polystyrene (about 80°C.), the looseness of packing of these polymers disappears and, consequently, at these temperatures there is no decrease in volume on mixing. The positive component of the heat of mixing accordingly disappears, so that the sign of the overall effect becomes negative. It is evident that, when solutions of polybutadiene are mixed with solutions of SKS-30 (or polystyrene) which have already undergone a decrease in volume during the process of solution, the heat effect on mixing is necessarily endothermic. From these considerations, it follows that mixtures of polybutadiene with SKS-30 or with polystyrene must exhibit a lower critical temperature of mixing in the neighborhood of 80°C. It must be borne in mind that any process involving a closer packing of the loosely packed polymer will decrease the positive component of the heat of mixing and hence will lower the critical temperature of mixing of the two polymers. In particular, such an effect is to be expected from the plasticizing of the loosely packed polymer by low-molecular solvents.

It should also be noted that, in the case of polymers with flexible molecules whose arrangement differs but little from that of their low-molecular polymer homologues, the heats of mixing of the polymers (per unit weight of the mixture) are the same as the heats of mixing of the corresponding hydrogenated monomers.¹⁶ Thus, the anomalies observed with polybutadiene-SKS-30 and polybutadiene-polystyrene systems are characteristic of loosely packed polymers, i.e., polymers with more rigid molecules. It is evident that, in such cases, the volume contraction and the corresponding heat effect may not be neglected in theoretical considerations.

In conclusion, we may touch upon some general problems whose detailed treatment lies outside the scope of this communication.

First of all, it should be noted that the application of thermodynamic relations and concepts (e.g., the concept of a phase) to systems in which the scale of heterogeneity is smaller than the length of the molecules requires serious critical analysis. This remark naturally applies not only to microheterogeneous polymer mixtures, but also to crystalline polymers which have recently been discussed in detail, particularly from this point of view.¹⁴ Furthermore, the loose packing of polymers may be either an equilibrium or a non-equilibrium property, which further limits the applicability of thermodynamic concepts to such polymers.

It should further be noted that, as it has recently been shown,^{14,16} in addition to the normal flow of polymers which takes place via the thermal motion of segments of the chain molecules, the application of great mechanical stresses may induce a flow by a second mechanism ("chemical flow"), which involves the rupture of chemical bonds in the molecular chain or network, displacement of the free radicals thus formed, and their recombination. Similarly, it is necessary to distinguish between mixing of two polymers which takes place without any alteration in the chemical structure of the polymer and that involving changes in the chemical structure and composition of the component molecules. Obviously, the formation of block and graft polymers by mechanical treatment is a special case of this second type of mixing. In this paper, only processes of mixing not involving appreciable changes in the chemical structure of the polymers have been considered. However, investigations by the author (together with E. V. Reztsova) have shown that mixing of two mutually insoluble polymers, when affected by the drastic action of mechanical factors and, hence, attended by chemical changes, may result in the disappearance of extremes on the property-composition curves and of phase separation normally observed with solutions of such polymer mixtures. It is evident that these changes, under such reaction conditions, are due to the formation of a single new copolymer from the two mixed components.

Finally, it should be noted that the problems connected with crystallization in mixtures of two polymers have not been touched upon in this paper.

References

1. V. A. Kargin, T. I. Sogolova, *Zhur. Fiz. Khim.*, **23**, 551 (1949).
2. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, 1953.
3. H. Tompa, *Polymer Solutions*, London, 1956.
4. R. L. Scott, *J. Chem. Phys.*, **17**, 279 (1949).
5. G. L. Slonimskii and N. F. Komskala, *Zhur. Fiz. Khim.*, **30**, 1746 (1956).
6. G. V. Struminskii and G. L. Slonimskii, *Zhur. Fiz. Khim.*, **30**, 1941 (1956).
7. A. Dobry and F. Boyer-Kawenoki, *J. Polymer Sci.*, **2**, 90 (1947).
8. H. Tompa, *Trans. Faraday Soc.*, **45**, 1142 (1949).
9. G. L. Slonimskii and G. V. Struminskii, *Zhur. Fiz. Khim.*, **30**, 2144 (1956).
10. N. F. Komskala and G. L. Slonimskii, *Zhur. Fiz. Khim.*, **30**, 1820 (1956).
11. A. A. Tager and V. A. Kargin, *Kolloid. Zhur.*, **14**, 367 (1952).
12. V. S. Klimenkov, V. A. Kargin, and A. I. Kitaigorodskii, *Zhur. Fiz. Khim.*, **27**, 1217 (1953).
13. V. A. Kargin, *J. Polymer Sci.*, **23**, 47 (1957).
14. V. A. Kargin and G. L. Slonimskii, *Uspekhi Khim.*, **24**, 785 (1955).
15. V. A. Kargin and T. I. Sogolova, *Doklady Akad. Nauk S.S.S.R.*, **108**, 662 (1956).
16. V. A. Kargin, T. I. Sogolova, G. L. Slonimskii, and E. V. Restova, *Zhur. Fiz. Khim.*, **36**, 1908 (1962).

Synopsis

Heats of mixing of polymers with each other have been measured, the behavior of the mixtures of solutions of various polymers has been studied, and the dependence of mechanical properties of polymer mixtures on the ratio of components has been investigated. It has been shown that mixing of polymers with each other is usually an endothermic process and, therefore, leads to formation of macroscopically homogeneous, but actually microheterogeneous, systems with an extremely high degree of dispersion. These polymer mixtures, which prevent macroscopic separation into phases but does not hinder the considerable mobility of the segments of flexible chain molecules. It has been shown that the dependence of mechanical properties of microheterogeneous polymer mixtures on the ratio of polymers in the mixture have sharp maxima which cannot be found in the case of true polymers in polymer solutions. It has been found that the behavior of some polymer pairs is anomalous, in that exothermal mixing is supplemented by separation of the solution mixture into two phases and by the appearance of maxima in the dependences of the properties of polymer mixtures on the ratio of polymers in the mixture. This anomaly has been attributed to the effect of loose packing of the molecules of the polymer which exists at a lower critical temperature of mixing whose value can be decreased by adding low-molecular solvents to the loosely packed polymer. Attention has been drawn to the fact that, although mixing of amorphous polymers should be considered on a thermodynamic basis to be a mutual solution of two liquid phases, the large dimensions and the flexibility of polymer chain molecules require a critical revision of the possibility of formal application of the basic thermodynamic concepts and relations to a theoretical analysis of the behavior of polymer mixtures.

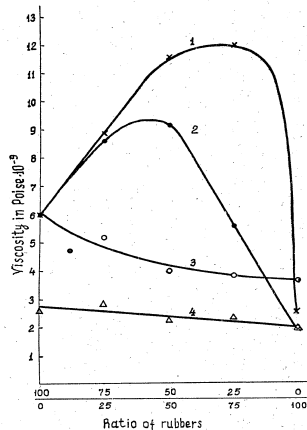


Fig. 6. Viscosity of rubber stocks prepared on the basis of combining two raw rubbers: (1) SKS-30 + SKB; (2) SKS-30 + NK; (3) SKS-30 + SKS-10; (4) SKB + NK.

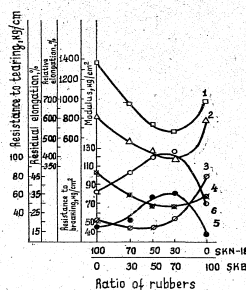


Fig. 1. Mechanical characteristics of combined rubbers prepared from mixtures of SKN-18 with SKB: (1) resistance to breaking; (2) relative elongation; (3) residual elongation; (4) resistance to tearing; (5) modulus at 200%; (6) modulus at 300%. Resistance to breaking is related to the cross section at the moment of rupture; the modulus at 200% and modulus at 300% designate stresses related to the initial cross section area at 200 and 300% elongation.

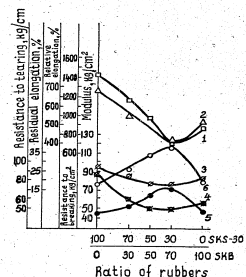


Fig. 2. Mechanical characteristics of combined rubbers prepared from mixtures of SKB with SKS-30: (1) resistance to breaking; (2) relative elongation; (3) residual elongation; (4) resistance to tearing; (5) modulus at 200%; (6) modulus at 300%.

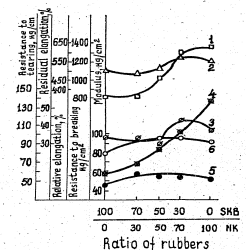


Fig. 3. Mechanical characteristics of combined rubbers prepared from mixtures of NK with SKB: (1) resistance to breaking; (2) relative elongation; (3) residual elongation; (4) resistance to tearing; (5) modulus at 200%; (6) modulus at 300%.

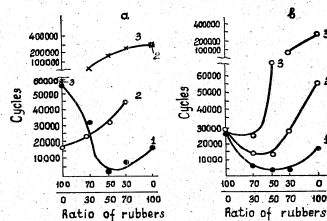


Fig. 4. Endurance of combined rubbers to multiple bending strain: (a) (1) SKS-30 + SKB; (2) SKB + NK; (3) SKS-30 + NK. (b) (1) SKN-18 + SKB; (2) SKN-18 + SKS-30; (3) SKN-18 + NK.

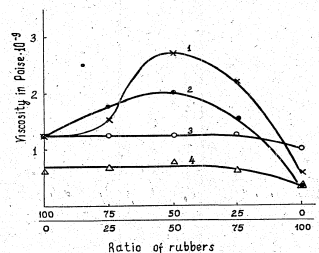


Fig. 5. Viscosity of raw rubber mixtures prepared on the basis of combining two raw rubbers: (1) SKS-30 + SKB; (2) SKS-30 + NK; (3) SKS-30 + SKS-10; (4) SKB + NK.